LUMINESCENCE

with particular reference to inorganic phosphors

A symposium held by the Electronics Group of The Institute of Physics
at the Cavendish Laboratory, Cambridge
from the 7 to 10 April, 1954

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SUPPLEMENT NO. 4

THE INSTITUTE OF PHYSICS, 47 BELGRAVE SQUARE, LONDON, S.W.1

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Foreword

The papers presented in this supplement, with the discussion on them, comprise the proceedings of a conference held in Cambridge on 7–10 April, 1954. The conference was organized by the Committee of the Electronics Group of The Institute of Physics, and was the first major discussion on the subject of luminescence since a conference held in Oxford in 1938; the emphasis was upon solid inorganic phosphors.

The papers were delivered in the form and order given here with the exception of the paper, "Some unsolved problems in luminescence", by Dr. J. W. Strange. This lecture was not suitable for reproduction in the form in which it was delivered in view of the many experimental illustrations; therefore only a summarized version is included in these proceedings.

Although the subject of luminescence may be of direct special interest to only a minority of scientists, the field of application is wide. This was indicated by the variety of firms represented at the conference and by the fact that more than one third of the individuals attending had come from overseas (from nine countries) to attend these meetings.

The Electronics Group wishes to record its most grateful thanks to Dr. S. T. Henderson, who acted as Honorary Conference Secretary, and Dr. G. F. J. Garlick for their unstinting help, particularly in the preparation of this supplement. The Group's thanks to the authors for their co-operation in the revision of manuscripts and to the editorial staff of the Institute are also recorded.

G. W. WARREN
Chairman
Electronics Group.

The Institute of Physics, London
October, 1954.

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The development of luminescence since the 1938 Oxford Conference

By S. T. Henderson, Ph.D., F.Inst.P., Thorn Electrical Industries Ltd., Enfield, Middlesex

A review of the state of knowledge of inorganic phosphors in 1938, and of the main practical and theoretical developments which have occurred up to the present time.

The Faraday Society's Discussion on luminescence at Oxford in 1938 was a very significant event. It had important effects on the development of the subject, though the immediate impetus it gave was mostly dissipated by the war which began so soon afterwards. Much of the work in Europe, and later in U.S.A., was then directed into the field of radar, with useful practical results no doubt, but with comparatively little advance of scientific knowledge when the wide scale of the effort is remembered.

Since the war progress has again been rapid, and we find ourselves now at the start of the first large scale conference on this subject to be held in Europe since 1938, and one which we may hope will settle some of our outstanding differences, and show the way to further advances; or, what is perhaps as important, help us to sort out what is significant in the great mass of new information, much of which is so difficult to fit into a coherent and progressive theory of luminescence. The purpose of this review is to emphasize those subjects which have received most attention in the past, those most active at present, and those we shall be concerned with during the next few days.

We may recall briefly the state of the art in 1938, but only so far as it concerns inorganic phosphors; at the present conference it has been necessary, for reasons of time, to omit any serious consideration of organic phosphors. In 1938, then, sulphides were the pre-eminent phosphors, deceptively simple in appearance, but as we have since found, having all kinds of hidden possibilities. Activation of zinc sulphide by excess of zinc was recognized as well as by silver, copper and manganese. The killers also were known, and their action, already put to practical use, was supposed to be due to a preferential trapping effect on electrons. In other phosphors manganese was the chief activator, as indeed it still is; but there was no clear indication that many new classes of compounds and unexpected activators might be found. The discovery about 1936 of zinc beryllium silicate was a portent of what was to come in the shape of new types of phosphor, and it was a notable achievement which no subsequent work has quite equalled. Sensitization had been recognized at about the same time, and the study of this widespread effect has had important consequences in both theory and practice. Theory of luminescence had developed by the configuration co-ordinate model (much used by photochemists), and by a simple version of the energy band model, and we find early references to those indispensable metastable levels or electron traps in crystal phosphors, which nowadays even phosphor chemists discuss with apparent unconcern. In 1938 the Frenkel exciton as a means of energy transport was being discussed. There was a considerable activity in discovering the exact form of decay curves, a subject which has declined in interest since those days, at least as an end in itself, though there are some specialized applications. Of present day interests which were well developed then, absorption and emission band measurements may be noted; but on the other hand there was not much recognition of the significance of temperature in phosphor work, whereas this particular tool is now seen to be of first importance.

On the practical side the cathode-ray tube was well established with many of its present phosphors, and a date worth remembering is 1936, when modern public television began in this country. Colour correction of high pressure mercury lamps by sulphide phosphors was beginning and, much more significant, cold-cathode sign tubing with neon or argon-mercury filling, and hot-cathode fluorescent lamps were under development. Another recently discovered technique with an unsuspected future was electroluminescence, which had to wait more than ten years for commercial exploitation.

We may say that at the time of the Oxford meeting few of our current problems and methods and theories had not been at least sketched in. The records of that meeting[1] are still interesting to read, and there are some striking predictions to be found in them.

The war period laid great emphasis on the cathode-ray tube, and we gained one useful class of phosphors with unusual decay characteristics, namely the fluorides. Also there was a new excitation method, the double-layer screen in which lower excitation densities were achieved by intermediate conversion of electron beam energy to blue light. Infra-red sensitive phosphors also received a great deal of attention during the war, following the timely recognition of the essential double activation of calcium sulphide to produce stimulation effects.[2] This injected new life into the moribund class of Lenard phosphors. In spite of much effort[3] and an interesting past history, they do not now seem to have any future importance. The radiochemical technique applied to them is not yet used as widely as it might be, and one of our papers at this conference will discuss it. Outside immediate military requirements there were also advances; an important practical one was the discovery of the halophosphates for lamp use,[4] and in the theoretical field came an extensive exposition of the relation between electron traps and thermoluminescence.[5] It is worth mentioning that the unique effect of traces of arsenic on the afterglow of zinc silicate was discovered in this period.[6]

The Cornell symposium of 1946 gave a useful cross-section of the subject at this point.[7] There was much emphasis on electron traps, on energy storage and release by infra-red, and on rate processes. The discussions dealt with a variety of topics, notably the use of energy level diagrams and the non-reproducibility of phosphor preparations.

Since the war substantial practical achievement has been accompanied by increasing complexity in every aspect of the subject. The cathode-ray tube still offers many problems. In particular, its requirements of fast-decaying phosphors for flying-spot transmission of film[8] and of resistant, non-saturating phosphors for projection-tube screens, to say nothing of colour components for colour television reception —these requirements do not seem to have been met entirely successfully. The more academic subject of electron penetration into phosphors is showing a welcome revival, and will be discussed at this conference.

As for phosphors usable in the low pressure mercury discharge, the supply continues unabated. It must be admitted that few of these new phosphors can compete with the established lamp phosphors. These discoveries are usually made by laborious (and expensive) search of small regions of

chemical composition. It is difficult to make sure in such work that no useful combination is missed as the systems become more complicated, often with four or five metals present in varied proportions. The position is somewhat similar to that in the field of metallic alloys; in both, complexity has led to new and unexpected achievements; in both, crystal structure determination is indispensable. It might be added that there is a further parallel in the comparative lack of theoretical basis in these two branches of science. This activity on behalf of the fluorescent lamp has been greater than for any other application of phosphors, which is reasonable when the scale of phosphor usage is considered.

One feature of recent progress in the discovery of new phosphors is the use of large proportions of structure modifiers like fluorine[9] and titanium[10]; especially remarkable is the introduction of alkali metals like lithium[11] and sodium.[12] Examples of mixed cations are far more numerous than of mixed anions: one recent example of the latter may be quoted.[13] New activators have appeared (trivalent cerium is a notable one), and others will be mentioned later. Of course, few of these complicated systems commend themselves to academic workers, who find sufficient problems in the simple oxides and halides which are generally of no practical importance in the applications mentioned.

In a period of rapid discovery it often happens that unfruitful work is abandoned for more rewarding topics, and much may be lost if the ground is not reworked. Surprising results have been obtained in research on inorganic phosphors by re-examination of old work in the light of greater experience or more subtle methods. There always seems to be something that was overlooked the first time. Another example depending on instrumental technique is infra-red emission, which has recently been found to occur among sulphides[14] and which will doubtless provide useful data for the theoretical aspects of luminescence.

When academic research seems to move slowly, rapid progress sometimes occurs under the stimulus of a commercial application. Electroluminescence provides an excellent example, in which practical developments of a spectacular kind have run ahead of theoretical explanations. We are, perhaps, at a point in time where useful discussion of the current theories can take place, probably not yet with finality since all the relevant facts are not yet established, e.g., the relative importance of surface and volume emission, and the effects of temperature. The brightness waveforms in electroluminescence have received much attention and discussion,[15] though without conclusive results; in the fluorescent lamp similar phenomena occur, and there might be some value in trying to associate the two cases. Electroluminescence underlines the comparative neglect of the electrical properties of phosphors generally, no doubt on account of the difficulties of measurement. It has now become essential to take account of dielectric properties, rectifier action and photoconductivity in electroluminescent phosphors. A very recent complication is electrothermoluminescence[16] with its analogy with the glow curve experiment, and, at the same time, its evident differences from that type of light emission. Incidentally, the glamour of the commercial application has tended to obscure the importance of silicon carbide and other semiconductors as electroluminescent crystals.

The best electroluminescent phosphors are doubly activated sulphides, which thus remind us of that very large body of experiment concerned with sensitized fluorescence in the most general sense, including quenching and stimulation by infra-red radiation, poisoning by transition and other elements (which may sometimes by contrast be activators), and nonlinear response to excitation, as well as the straightforward cases such as calcium silicate activated with lead and manganese (which has become a common lamp phosphor). It may be doubted if the effects of sensitization can ever be entirely removed from phosphors, simply for reasons of the limitations of chemical purity. The present theoretical conception of phosphors owes much to the study of sensitization in its different manifestations. There are many difficulties and insufficiencies remaining in this aspect of luminescence, and for all our assumptions of electron transitions, positive hole migration, trapping and retrapping, our models still seem rather crude and need frequent revision as new facts appear; but we have at least a framework which roughly contains some of the facts. Our two theoretical models are mutually exclusive, and each makes untrue simplifying assumptions: the configuration co-ordinate model neglects energy transport, while the energy band diagram neglects atomic rearrangements; hence some of the difficulties.

Contributing to the general theoretical picture in a notable way is thermoluminescence, and other experiments using the temperature parameter. Electron trapping and hole migration have been extensively studied by these methods. Interpretations vary, as usual, with the appearance of new information. Thus, in sulphides the limitations of the glow curve are being realized as regards revealing trap distributions,[17] though it may be said that traps are becoming slightly more clearly defined from the chemical viewpoint. Energy transport is another aspect of phosphor behaviour which was being discussed in 1938; it has recently been thoroughly examined from the resonance angle.[18] It is particularly important in sensitized or doubly activated materials and we shall give some time to it in our discussions. Although outside our present scope, a reference must be made to the use of organic liquids as scintillators, where energy transport is an essential feature.

Spectral bands of excitation, absorption and emission have received much attention, though to different degrees. Emission bands in particular have practical importance, can be studied fairly easily, and moreover have a certain aesthetic attraction which may have helped to ensure the constant popularity of this sort of work. Continuing problems are the significance of sub-band structure and multiple bands, and the constancy of band position within limited changes of phosphor composition. Infra-red bands have already been mentioned, and the range of luminescence has been extended into the ultra-violet region by many examples. Of special interest is the red band spectrum of manganese—activated magnesium compounds (oxide, arsenate, germanate and antimonate). The configuration co-ordinate model has been applied with some success to the problem of the shape of emission bands.[19]

Perhaps the most important mystery which we are trying to probe is the nature of the luminescence centre, its energy levels and its atomic constitution. This involves all the current theoretical ideas, but it is susceptible of attack by a variety of experimental methods without too much dependence on a particular model. At the moment, after years of rather ineffectual speculation, converging ideas on the centre are coming to a very rough kind of focus. There is still much variety of treatment, a recent hopeful line being the relegation of the activator ion itself to a secondary role.[20] From the combined evidence of temperature effects, emission bands, magnetic properties, efficiency measurements and X-ray structure determinations, we may hope soon to arrive at a consistent picture which will suggest further advances. After

all, it is not really essential to know exactly what the centre is, any more than we need to know what the electron is. We chiefly want to know how it works. Recent work with an emphasis on crystallographic structure offers useful lines of thought,[21] and extension of such methods is desirable.

Turning to a more concrete subject, namely the zinc sulphide phosphors, we may note how experiment on physico-chemical lines has produced a remarkable expansion in knowledge. This is largely due to the work of the Eindhoven laboratories. So far from presenting the completed picture we imagined in 1938, these phosphors now seem to have unlimited possibilities. Activators and co-activators like lead, oxygen, sodium, lithium, chlorine, cerium (3+), aluminium, and scandium have been introduced. Other workers have added phosphorus, arsenic, terbium[22] and tin to this list, and have shown besides how to increase the useful content of foreign metals to a large degree.[23] The idea of charge compensation built up by this work has another important application in the controlled valency semi-conductors.[24] Speculations on the nature of the emitting centre in sulphides have been unrestrained, and there are numerous proposals for the centre responsible for the green emission of ZnS . Cu. These include interstitial copper atoms and cuprous ions, substitutional cuprous and cupric ions, and cupric ions with oxygen neighbours. The blue band has a corresponding array claimed for it, including some of those mentioned for the green band. Perhaps earlier remarks on our improving knowledge of the centre were a little optimistic in view of this wealth of invention.

A less controversial matter is the use of single crystals of phosphors for measurement of optical, electrical and thermal properties. The value of this was foreseen in 1938, though only halide crystals of any size were then available. So far, little use has been made of the possibilities except for scintillation counting, beginning about 1944. This is largely concerned with organic crystals; apart from these, sulphides, tungstates and halides are all used, either for α-, β- or γ-rays. The value of isolating single particle or quantum effects is evident, also of avoiding the confusing effects of microcrystalline layers on quantitative determinations. Recent examples of single-crystal work include studies of cathode-ray absorption,[25] of electroluminescence,[26] and of infra-red absorption.[27] It might be of interest to examine any possible application of dislocation ideas to these phosphor crystals.

Finally, some comment is necessary on the more rarefied theoretical work that has been done on luminescence. It may be emphasized that the subject is still very largely an experimental science, if not a craft. However, the reader of the literature of luminescence is now being presented with formidable mathematical developments in which the basic experimental facts seem to carry a very heavy superstructure, and there are some differences of opinion among us as to the value which this kind of work has for the explanation or interpretation of the subject. There can be little disagreement with the position expressed by Whitehead, himself a mathematician, who said that there can be no true physical science which looks first to mathematics for the provision of a conceptual model. In any case, the phenomena of luminescence arise in imperfect crystal lattices which cannot be treated by first principles with any hope of deducing such complicated patterns of behaviour as those we observe. Experimental results must, therefore, be used to a greater or less extent in the theoretical treatment, but it is possible that unconscious interpretations of the facts may be injected at the same time, and this is a danger to be borne in mind. Thus, to say that these mathematical derivations are most successful when the answer is known beforehand may be a cynical comment, but it contains a grain of truth. The real test of value, as always, is whether the theoretical conclusions lead on to new experiment, or are treated as ends in themselves; whether in fact a theory is regarded as a policy or a creed. In one sense workers in this field have a harder task to justify what they do than laboratory workers in luminescence, for we tend to be less critical with regard to empirical discoveries of new facts, however useless they may be. It is evidently most important to maintain understanding and co-operation between the parties, for both can promote the advance of knowledge in this field.

It is premature at this moment to demand the prediction of an entirely new luminescent system as a test of the validity of the theoretical approach. This would, of course, be an achievement worthy of great efforts by the mathematical physicist, and the challenge has already been accepted in principle by Williams,[28] whose work in this field is outstanding.[29] In 1938 Seitz put one of the principal purposes of a theory of luminescence at the more modest level of providing an atomic picture of the centres. We may perhaps agree on that as a reasonable objective for the present.

This review has omitted many applications of luminescence and its relations to other solid state processes, for example, to photography. Such correlations are likely to be of great value, but cannot be pursued in a general survey. However, most of the important lines of development have been covered, and if our discussions in Cambridge lead to greater understanding of some of them, the conference will certainly have been worth while.

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Some unsolved problems in luminescence

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The purpose of this lecture and demonstration, of which this is a summary, was to demonstrate and discuss some of the fairly well-defined phenomena which need explanation by any comprehensive theory of luminescence.

1. *Importance of method of preparation*

Most phosphors are synthesized by solid state reactions. A phosphor such as zinc silicate activated by manganese may suffer profound changes according to the order in which these reactions take place.

Two similar zinc silicate phosphors were shown, made with identical starting materials. The short decay material was made by mixing all the components before heating. The long decay material resulted from preheating the zinc and manganese components to form the spinel $ZnMn_2O_4$.

Other samples shown, of widely different fluorescence colours, had been prepared during experiments on potassium additions to zinc beryllium silicate.

2. *Importance of imperfections*

One point very seldom recognized in the theoretical approach is the importance of non-stoichiometric proportions, for in almost all cases the optimum efficiency is attained with excess of one or other component. Calcium silicate, zinc silicate and the halophosphates are all improved by an excess of acid radical; a few, like the tungstates, are improved by an excess of basic oxide. This suggests that luminescence does not arise in perfect crystal forms, but is associated with imperfections and dislocations in crystals. There are consequently very few vitreous phosphors, and after melting many phosphors become nearly or quite non-luminescent. Cadmium borate is an example.

3. *Activators*

The importance of a small proportion of metal impurity in promoting luminescence is one of the best known facts, but why is Mn so unique an activator? Why is Cu effective in percentages as low as 0·01% while Mn requires 0·1–5%, and Ti is effective up to 10% in some lamp phosphors and at much lower concentrations in cathodoluminescent materials? Are activators always present or are there "pure" phosphors? These questions still await answers.

4. *Influence of other impurities*

Additions far smaller than those of the activators may induce long phosphorescence or decrease the efficiency of fluorescence. The increased phosphorescence of zinc silicate containing 10^{-5} of arsenic was demonstrated. Nickel has a similar effect in zinc borate (though at higher concentrations); but in ZnS.Cu, nickel has a quenching effect on phosphorescence at very low concentrations. Iron reduces phosphorescent decay and also efficiency in ZnS.Cu, but in cadmium borate it causes a slow build-up of emission accompanied by loss of efficiency. This was shown by comparison with a normal sample, both previously heated to a high temperature to expel any stored energy. The long blue afterglow of the internal silica coating in an incandescent lamp was also demonstrated. This may possibly be due to incomplete dehydration of silica in the manufacture.

5. *Storage and ejection of trapped electrons*

Three phosphors were shown with very similar glow curves, but very different response to infra-red radiation. The first, ZnS.Cu without other addition, showed the initial increase of afterglow followed by exhaustion. The second sample contained 10^{-5} of iron and 10^{-4} of copper activator. Infra-red radiation in this case caused immediate quenching of the afterglow. In the third sample where lead replaced the iron, infra-red stimulation produced strong enhancement of the afterglow with eventual exhaustion.

6. *Stimulation*

Three samples were shown, SrS.Ce, Sm, SrS.Eu, Sm, and SrS.SrSe.Ce, Sm, in which the secondary activator samarium was responsible for storage effects. Under short ultra-violet radiation little fluorescence was apparent but with subsequent infra-red stimulation bright emission occurred, green, orange and yellow respectively.

7. *Low temperature storage effects*

Excitation at liquid air temperature may often cause energy storage and on warming to room temperatures this may be released rapidly (the glow experiment). As an example $CaTiO_3$.Pr was shown, giving a bright red emission.

8. *Re-trapping of electrons*

The sample of ZnS.Cu, Pb mentioned above was used to demonstrate re-trapping. The phosphor was excited at room temperature, cooled to 90° K and allowed to warm up. Very little phosphorescence was observed below room temperature owing to the presence of most of the excited electrons in deep traps. In a second experiment the same phosphor was excited and cooled as before, then irradiated with infra-red radiation at 90° K. This causes the ejection of some electrons from deep traps and their re-trapping in shallower traps, from which they are readily released; thermal glow was observed almost continuously when the sample was warmed up to room temperature.

9. *Deep traps*

Traps are present in a wide variety of other phosphors without long apparent phosphorescence, and often the traps become filled almost immediately after preparation and are only emptied at high temperatures. Examples are cadmium borate and calcium and cadmium silicates. The effect was seen by taking a plate coated with cadmium borate, previously heated to about 500° C and stored in the dark, and exposing it to 2537 Å radiation, first with one half covered and then with the covering removed. A marked colour and intensity difference between the two sides was observed followed by a rapid build-up to equality. Shallow traps in this material indicate their presence by a typical glow curve, but transfers from the deeper traps are non-radiative because of temperature quenching.

Another effect was demonstrated by a cadmium borate fluorescent lamp. After operation on a normal circuit, exposure to visible light or 3650 Å radiation produced a short-lived phosphorescence.

10. *Cascade excitation*

An explanation of the last experiment might be cascade excitation. A much more striking example is a phosphor of composition $5CaO.3Al_2O_3$ with about 1% Tl added before firing at 1250° C. When exposed to sources of either 2537 Å or 3650 Å radiation only a feeble fluorescence resulted, but exposure to 2537 Å, even for a few seconds, followed by exposure to 3650 Å radiation, produced a bright yellow fluorescence.

11. *Radiophotoluminescence*

This calcium aluminate phosphor showed a similar effect if excited first by X-rays, and then by 3650 Å radiation, as in the well-known phenomenon of radiophotoluminescence. A similar effect referred to by Mr. Hill in his paper was also demonstrated; in this, screens of manganese-activated fluorides were shown to fluoresce under ultra-violet excitation in the regions which had been scanned previously by a cathode-ray beam.

12. *Multi-colour glow curves*

The last sample demonstrated was cadmium phosphate activated by lead, which has a blue fluorescence and afterglow. When excited at low temperature and warmed to room temperature it shows a blue glow, but when excited at room temperature and heated, it shows a striking succession of peaks, in the order blue, red, blue, followed by a number of distinct orange peaks.

Acknowledgements

Thanks are due to those who contributed samples and help with the demonstrations, in particular to Dr. Garlick, Mr. Hill, Dr. Ranby, Dr. Henderson and Mr. Rice.

Paper 1

Applied cathodoluminescence

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The classes of phosphor in commercial use at the present time comprise the zinc and cadmium sulphides, the manganese-activated silicates, titanium- and cerium-activated calcium magnesium silicates, the manganese-activated fluorides and zinc oxide. Each is limited to particular operating conditions. Attempts to produce a phosphor emitting white light with an efficiency comparable with that of a mixture of blue and yellow emitting sulphides have met with only partial success.

The intrinsic efficiency of cathodoluminescent materials increases with the bombarding voltage up to about 25 kV but decreases in all cases at very high intensities of excitation. The maximum efficiencies so far observed are about 23% for zinc sulphide phosphors and about 8% for other types, or between $\frac{1}{3}$ and $\frac{1}{4}$ of the maximum efficiencies of the same phosphors under ultra-violet excitation. Recent work on single crystals, showing the limitations of the Thomson–Whiddington law, is relevant to the question of efficiency.

Practical cathode-ray tube screens exhibit much lower luminous efficiencies chiefly owing to the fact that they are viewed from the opposite side from that excited. Other losses arise from the sensitivity of the phosphor to the manufacturing processes. Little is known of the mechanism by which the efficiency of a screen falls during life but it appears that electron bombardment creates new centres of various kinds; for example a new sensitivity to ultra-violet excitation is produced in the fluoride phosphors.

In reviewing the field of applied cathodoluminescence, the intention is to present a broad outline of the types of phosphor in general use, their intrinsic efficiencies as convertors of electron energy into radiation, and the efficiencies realized in practical tubes. Space does not permit of any consideration of cathode-ray excited phosphorescence.

The cathode-ray tube is now some thirty years old. Over the last ten years there have been surprisingly few additions to the list of practical cathodoluminescent phosphors. Even the stimulus of wartime radar research has produced only one new class of materials, the Group 2 fluorides. Many thousands of substances have been tried, but very few have proved to be of value. Improvements in well-tried phosphors have more than kept pace with any new materials that have been proposed.

PHOSPHORS

The classes of material are summarized below. This list is not exhaustive but covers most of the phosphors in commercial use.

Zinc and cadmium sulphides. These well-known materials have the highest observed efficiencies and provide a range of colour throughout the spectrum. Their chief limitations are saturation of light output at high current densities, relatively low "sticking" voltage, high sensitivity to contamination during tube processing and, in some cases, considerable body colour (absorption of visible radiation). Their decay characteristics are complex, consisting in general of an initial rapid process, dependent on the exciting intensity and lasting from 10 to 100 μsec followed by a slow, strongly temperature dependent process which is readily saturated and which may continue for hours. The second process is subject to some control during the phosphor manufacture.

Manganese-activated silicates. The zinc and zinc beryllium silicates are the only members of this class in general use. They have about half the efficiency of the sulphides but do not show such severe current saturation. Their secondary emission properties are slightly better than the sulphides and they are much less sensitive to tube processing. Colours from green to orange can be obtained. The initial decay process is exponential with a time constant of about 10 msec, independent of the exciting intensity, and is followed by one or more slower, temperature dependent processes. Again, the latter are to some extent under control during manufacture.

Calcium magnesium silicates. This new class of phosphor has appeared since the war.[1] Two members are of some importance. Diopside ($CaO.MgO.2SiO_2$) activated with titanium provides a broad blue emission. It shows less current saturation than the sulphides and is more robust although it has only half their efficiency. Its initial decay process is similar to that of the sulphides, but is not intensity dependent. There is sometimes a slow process of low intensity which may persist for minutes.

Akermanite ($2CaO.MgO.2SiO_2$) activated with cerium emits in the near ultra-violet and violet regions, with a relatively low efficiency. Its value depends on the very rapid decay, independent of intensity, which has a constant of the order of 1 μsec or less.

Manganese-activated Group 2 fluorides. This extensive class of phosphors arose out of the need for long afterglows in radar screens. Phosphors based on both the rutile and perovskite type of fluoride have been used. Examples are ZnF_2 activated with manganese and $KMgF_3$ activated with manganese and containing some ZnF_2 in solid solution. These materials exhibit a relatively slow initial decay process with a time constant of the order of 1/10 sec followed by one or more temperature dependent processes which may persist for minutes.

Zinc oxide. Zinc oxide still finds some application as a short afterglow phosphor. Two emissions may be obtained. An ultra-violet emission at about 3900 Å has a very rapid decay of the order of 10^{-7} sec and a low efficiency, while a yellow-green emission at about 5000 Å decays in a few microseconds and has an efficiency comparable with the manganese-activated silicates. Both forms are susceptible to burning during life.

RECENT DEVELOPMENTS

As will be seen below, the efficiencies of current phosphors are surprisingly high, and it is to the secondary characteristics such as stability, body colour, and afterglow control of known materials that most research is now directed. In work of this kind the requirements of the particular application are paramount, and few generalizations are possible. It may be

of interest, however, to refer briefly to one example of a search for a phosphor to fill a particular requirement, which, while it has not been conspicuously successful, has resulted in the preparation of a number of interesting materials. The problem was to find a so-called "single component" white phosphor for direct-viewing television screens.

The present sulphide mixture not only has a high intrinsic efficiency but produces white light with the most efficient pair of complementary colours.[2] Any single component phosphor must have a comparable luminous efficiency. Attention has, therefore, been concentrated on the production of two suitably placed emission bands in the same zinc or zinc–cadmium sulphide base.

Several attempts have been made[3–6] to combine in one phosphor the emissions due to gold, phosphorus or arsenic with the blue emission of silver- or zinc-activated zinc sulphide.

In all these materials control of the fluorescence colour demands very close control of the ratios of the effective concentrations of the two activators. This may be related to recent work on the photoluminescence of sulphides,[7–9] which has drawn attention to the fact that the partition of absorbed energy between the different types of centre, present in one phosphor, is a complex dynamic process.

The activator concentrations in normal sulphide phosphors are very low. About 50 parts per million of silver are added to ZnS to give the normal blue component, but under commercial manufacturing conditions the fraction of this amount which is effective in the finished phosphor is somewhat indefinite. In a singly-activated material this does not matter because a small variation will only affect the amount of current saturation, and even this is not very sensitive to such variations.

Clearly, therefore, even if all the secondary properties of these multi-activated sulphides were satisfactory, the task of manufacturing them presents very much greater difficulty than the blending of two or three separate phosphors in more or less equal amounts in order to obtain a screen of the desired colour. In fact the materials so far produced all show various additional shortcomings compared with normal mixed phosphor for television picture tubes.

THE INTRINSIC EFFICIENCY

Very few direct determinations of the intrinsic efficiency have been made for cathodoluminescence, although there have beeen numerous estimates based on a variety of assumptions. Furthermore, there are wide discrepancies among the results obtained by different workers. Probably the most reliable data available today are those of Bril and Klasens[10] and of Hopkinson.[11] Bril and Klasens found that the efficiency of all the phosphors measured increased with the bombarding voltage up to about 20 kV, but varied only slightly between 20 and 40 kV. Much of the earlier work was concerned with the range 1 to 10 kV. In this range Hopkinson found in general an increase in efficiency with voltage, as did Strange and Henderson[12] and many others.

The relation between light output and voltage in this range has been fitted empirically to an expression of the type

$$L = K(V - V_0)^q f(i)$$

where K, V_0 and q are constants for a given specimen and $f(i)$ is some function of the current density. Values of q between 1·0 and 3·0 have been found by various workers although a figure close to 2 is fairly common, and with this value the efficiency is a linear function of the voltage. Dowling and Sewell[13] recently found the efficiency to be constant from about 2·5 kV to 20 kV fo rseveral phosphors.

The energy efficiencies of the principal types of phosphor as found by Bril and Klasens at 20 kV are given in Table 1.

Table 1. *Intrinsic efficiencies of various phosphors at 20 kV*

Phosphor	*Activator*	*Intrinsic efficiency (%)*	*Lumens/watt*
ZnS ZnS.CdS	Various (Cu, Ag, Zn)	18–25	7–100
Zn_2SiO_4	Mn	8·5	40
$CaO.MgO.2SiO_2$	Ti	7·5	5
ZnO	Zn	7·5	4

These figures were determined with a stationary beam of low current density (1 μA/cm^2) on thick layers of phosphor on a metal support, with corrections for self-absorption of the emitted light in the phosphor layer. Hopkinson's results were obtained with a slightly defocused television raster at 0·01 μA/cm^2, and so cannot be compared directly with the preceding case.

In deriving these figures Bril and Klasens made the assumption that "all the energy of the primary electrons is absorbed by the phosphor." It now appears possible that for the lower voltages this assumption is not justified. So far no direct measurement of the energy dissipated by secondary electrons from phosphors in this voltage range has been made, but the elegant experiments of Ehrenberg and Franks[14] suggest that for conventional phosphors the fraction lost in this way may be considerable for voltages below 20 kV.

Ehrenberg and Franks have taken microphotographs of the glow emitted by single crystals of calcium and cadmium tungstate and of several halide phosphors during bombardment by a fine pencil of electrons. The beam was normal to the crystal surface and the glow was observed in a direction parallel to the surface. Accelerating voltages from 2 to 40 kV were used. For dense materials and low voltages the glow occupied a hemisphere centred on the point of entry of the beam, but for higher voltages or less dense materials the centre of the glow moved into the crystal so that at a high enough voltage it occupied a full sphere. This suggests that in the range in which the glow is hemispherical a large fraction of the primary energy is lost as fast secondaries, and that as the penetration increases an increasing fraction of the primary energy is dissipated within the crystal. If this is the case then an increase in efficiency with voltage is to be expected, but the exact form of the relation will be complex and will depend on the nature of the phosphor layer. With a rough surface some of the fast secondaries will excite neighbouring particles, and few of the primaries will strike the crystal surface normally. The ranges observed by Ehrenberg and Franks, particularly at the lower voltages, were considerably greater than those deduced by other workers from the application of the Thomson–Whiddington law,

$$R = bd^{-1}V^2$$

(where R is the range and d the density of the solid, using Terrill's value[15] of the constant b), or from the observed relation between light output and voltage of both powdered layers and evaporated phosphors.[13, 16] As Garlick has pointed out,[17] the Thomson–Whiddington law applies to unscattered electrons and its experimental basis is the penetration of metal foils by beams of high velocity (50 kV). The ranges observed by Ehrenberg and Franks were clearly those of scattered electrons, and it is these that are relevant to any consideration of the mechanism of cathodoluminescence. Until the questions raised by this work are settled the usual

invocation of "dead" surface layers to explain the form of the relation between voltage and efficiency seems somewhat unnecessary.

On the relation between efficiency and current density a number of contradictory statements have appeared in the literature, but in this case the discrepancies can usually be resolved. In nearly every practical case the phosphor is scanned by a fine electron beam so that each crystal receives short pulses of excitation at a high instantaneous current density although the average current density over long periods may be quite low. Many measurements have also been made with stationary beams. The behaviour of a phosphor may be very different in the two cases. In a television raster the instantaneous current density may be between 10^5 and 10^6 times the average value. Considering first the case of continuous excitation we find that at very low current densities the light output is proportional to the current, although in certain sulphide phosphors Lasof[18] has shown that there may be a region in which the efficiency increases with current density. This behaviour is similar to that observed with ultra-violet excitation of low intensity[7,9,19] and is a consequence of the partition of energy between centres of different kinds discussed by Klasens.[7] As the current density is increased there comes a point at which the efficiency begins to decrease and eventually the light output may become saturated, although the cases in which this happens at currents low enough to avoid excessive heating of the phosphor are rare. In the case of discontinuous excitation much the same sequence of events is found, but the level at which the efficiency begins to fall off will differ from that for continuous excitation of the same phosphor.

All these phenomena have been satisfactorily explained by consideration of the occupancy of the available luminescence centres. Bril[20] has in fact used this treatment to estimate the numbers of effective centres in various phosphors. The case of greatest practical importance is the relative behaviour of sulphide and silicate phosphors. The former phosphors, having a low concentration of centres and a fast decay process show severe saturation under normal scanning conditions but little or none under continuous excitation of the same average current density. The silicate phosphors can be made with much higher activator concentrations, but have longer decay times. Under normal scanning conditions, when the excitation frequency is comparable with the decay time, they do not saturate until considerably higher average current densities are reached than for the sulphides, but under continuous excitation their saturation occurs at about the same current density as when scanned.

It is of some interest to compare the efficiency of phosphors excited by cathode-rays with their efficiency under ultra-violet radiation. Most previous authors have made this comparison with figures for excitation by electrons of 1 to 10 kV energy, but it is now possible to use figures obtained at a voltage where the efficiency is no longer increasing with voltage. The phosphors with which we are concerned generally show a quantum efficiency close to unity for optical excitation so that their energy efficiency will be greatest for excitation by the longest wavelength for which the quantum efficiency remains at this figure. Unfortunately, reliable data on this point are surprisingly scarce. The figures quoted by Bril and Klasens[10] for the efficiency of several zinc sulphide phosphors under 3650 Å radiation appear to be much too low, implying a quantum efficiency of less than 0·5. The relative cathode-ray efficiencies of the three sulphides quoted are very probably in the same sequence as their ultra-violet efficiencies, as shown in Table 2, where an estimate has been made from various sources of the long wavelength limit of the excitation spectrum, and the optical efficiency calculated on the assumption of unit quantum efficiency.

Table 2. *Comparison of phosphor efficiencies under cathode-ray and ultra-violet excitation*

Phosphor	*Cathode-ray[10] efficiency at 20 kV* %	*Excitation limit* (Å)	*Emission peak* (Å)	*Optical efficiency assuming Q.E. = 1* (%)	*Ratio of optical to c.r. efficiency*
ZnS.Ag	23	3650	4490	82	3·5
ZnS.Zn	17	3450[21]	4650	74	4·4
ZnS.Cu	18	4000	5290	76	4·3
Zn_2SiO_4.Mn	8·5	2600	5250	49	5·8

Only by comparing the cathode-ray efficiencies with the optical efficiencies at the longest wavelength of efficient optical excitation can any estimate be made of the efficiency with which energy is transferred from the bulk of the lattice to the luminescent centres. It would be of considerable interest to make such comparisons with some of the doubly-activated or sensitized phosphors used in fluorescent lamps. Little information is available, but in most cases cathode-ray bombardment excites the centres emitting at longer wavelengths (usually manganese) more strongly than those emitting at shorter wavelengths (usually lead, antimony or tin).

SCREEN EFFICIENCIES

Turning now to the efficiencies realized in normal cathode-ray tube screens, it is apparent that since these screens are viewed from the side remote from the exciting beam their efficiencies simply as light sources will not approach the intrinsic efficiencies of the phosphor crystals. The principal factors, namely screen thickness and self-absorption of the emitted light, particle size, and the effects of binders, have been dealt with both theoretically and experimentally by various workers.[10,11,22,23] Longini's work may be particularly emphasized.[22] Hopkinson[11] described a detailed experimental approach to the problem of defining optically the parameters for optimum screen efficiency, and Bril and Klasens[10] discussed the gain to be expected by the current practice of aluminizing. It appears that at the optimum thickness of a non-aluminized screen, about one-third of the light is emitted in the forward direction. With an aluminium layer of 80% reflectivity this figure can be increased to something over two-thirds. However, few practical screens show efficiencies of the order to be expected on this basis. Sulphide screens in particular suffer a depreciation of 10 to 20% in the course of normal screen laying and tube processing. With silicate screens this loss is much less.

Inadequate secondary emission and consequent screen "sticking" under bombarding voltages above about 12 kV was at one time a serious cause of low efficiencies. This has been completely eliminated by the practice of aluminizing, or partially overcome by the addition of various materials to the screen.[24] The efficiency of this latter method seems to depend on the conditions under which the screen is laid, but when properly operated an increase of 3 to 4 kV is observed in the voltage at which a sulphide screen can be run.

In contrast to the case of fluorescent lighting, there appears to be a considerable reluctance to publish details of the efficiency of commercial cathode-ray screens. Some figures are given in Table 3, but it is possible that some current tubes will show higher efficiencies.

Table 3. *Luminous efficiencies of some cathode-ray tube screens*

Phosphor	*kV*	*Method of excitation*	*Efficiency (lumens/watt)* *Non-aluminized*	*Aluminized*	*Colour*	*Reference*
Zn_2SiO_4.Mn	10	Static		24	Green	25
	15	Static		38	Green	25
	6	Television raster (60 c/s)	8		Green	26
	6	Television raster (50 c/s defocused)	12		Green	11
ZnS.Ag	6	Television raster (60 c/s)	6		Blue	26
ZnS.CdS.Ag + ZnS.Ag	6	Television raster (60 c/s)	14		White	26
"	10	Television raster (50 c/s)		31	White	28
ZnS.CdS.Zn + ZnS.Ag	10	Television raster (50 c/s)		25	White	28

SCREEN BURNING

The deterioration of a cathode-ray screen during life is generally referred to as "burning." Many different types of burn can be distinguished, some of which may be attributed to the special circumstances arising in particular tubes.

Both negative and positive ions may be accelerated towards the screen and both cause some destruction of the luminescent properties in the surface layers of phosphor. A fairly complete study of the nature and origins of these ions has been made by Bachman, Hall and Silberg.[27] Little is known, however, of the relative resistance of different phosphors.

Of greater interest is the deterioration caused by electron bombardment. This may consist simply of a drop in luminescence efficiency, or it may be accompanied by the development of a visible absorption. The secondary emission coefficient of most phosphors also falls during life and this may cause an additional loss of light output. The rate of burn varies widely from phosphor to phosphor, and is also dependent on the treatment during screen laying and tube processing. Very little systematic work has been done on this subject although an understanding of the mechanism would be of great value.

In the case of the sulphide phosphors there is a close connexion between the electron burn and the blackening produced by exposure to light and moisture. Material that has undergone some photolysis burns more rapidly than material that has not. The reduction in efficiency, however, is not confined to the surface layers, being equally evident over a wide range of subsequent bombarding voltages.

The long-afterglow fluoride phosphors show some remarkable features during life. The phosphorescence is affected much more strongly than the fluorescence and at the same time the material becomes sensitized to ultra-violet excitation. A part of the light emitted under ultra-violet excitation arises from energy stored in deep traps, but the sensitivity remains after this source has been exhausted, for example by heating to about 400° C.

It appears, therefore, that electron bombardment can produce new kinds of "centre" in a phosphor. Whether this occurs in an "ideal" crystal, or only in the neighbourhood of particular lattice defects or impurities, is not known.

An investigation of these phenomena under well-defined conditions would probably be most rewarding and might throw useful light on the kindred problems of photolysis, the coloration of alkali halides and the photographic process.

CONCLUSION

In conclusion, it may be emphasized that a wealth of fundamental work remains to be done in the field of cathodoluminescence. This work will be rewarding not only to those directly concerned with the mechanism of the luminescence of solids, and its applications, but also to those whose interest is in the more general behaviour of insulating crystals under electron bombardment. Now that it is possible to produce fairly well-defined phosphors in the form of single crystals progress should be rapid.

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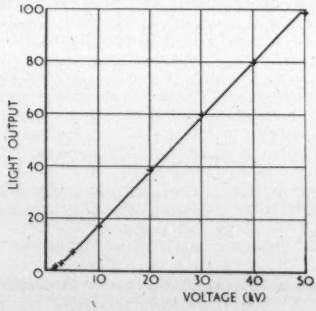
DISCUSSION

Dr. A. Bril: The difference between the measured and intrinsic efficiencies in our measurements referred only to absorption and scattering of the fluorescent light by the phosphor grains. No corrections were made for elastically or inelastically scattered electrons. Measurements of some authors[1] show that the relative number of back-scattered electrons for aluminium is about 15–20% for 20 kV. These values may be valid for O- and S-dominated phosphors in single crystal form, but for a powder layer electrons scattered by one particle will be absorbed by another. Thus we expect that up to 20 kV the correction is far less than would follow from experiments on single crystals,[2] and on metals.

The apparent discrepancy between the measurements of Dowling and Sewell and our own is due to the different methods of plotting results. Dowling and Sewell plotted light output *versus* voltage, but we have plotted efficiency *versus* voltage. Up to 50 kV our measurements indicate a linear relation between brightness and voltage except for the first few kilovolts, as shown in the figure which presents our earlier data.[2]



Variation of light output of $Zn_2SiO_4.Mn$ with voltage of cathode-ray tube beam

We found for the efficiency of a non-aluminized screen (ZnS.Ag and unactivated ZnS.CdS) 12 lm/W, which agrees well with measurements on thick layers[2] and with the values given by Hopkinson and by Leverenz.

Dr. S. T. Henderson: It is interesting to consider the the similarities between the radiophotoluminescence of NaCl.Ag,[3] of the KBaAlAg phosphate glass,[4] of the fluorides exposed to cathode rays,[5] and of the calcium aluminate activated by thallium.[5,6] All these materials show a sensitivity to one type of excitation induced by a previous small exposure to a different kind of radiation, though there are differences of degree, and possibly of kind, in the various responses.

Dr. G. R. Fonda: It is often held that the mechanism of of screen deterioration lies in a chemical decomposition. Hanle and Rau[7] have drawn attention to lattice displacements produced by impinging ions as a result of elastic collisions. They found that the reduction of efficiency in a phosphor bombarded by hydrogen and rare gas ions in a uniform field increased with the ionic mass. One might infer that the same effect is produced by electron bombardment but at a rate very much inferior to that for ions, and also that the phosphor efficiency may be a function of the number of lattice displacements.

Dr. H. A. Klasens: The author questions our figures for the efficiency of ZnS phosphors under ultra-violet excitation because they imply efficiencies of less than 50%, but this is the correct conclusion. Botden has measured the quantum efficiencies of a large number of phosphors from various sources and finds that while with oxygen-dominated phosphors quantum efficiencies approaching 100% are obtained, the efficiencies for sulphides rarely exceed 50%. Few data are available, for example, those of Schmieder,[8] but he measured the quantum efficiency of build-up of the light sum and in interpreting the data used Lenard's theory of phosphorescence centres (Dauerzentren) which is not now acceptable. The most reliable direct measurements[9] for a ZnS.Cu phosphor gave a maximum efficiency of 50% at 3600 Å. The low quantum efficiency is probably due to absorptions corresponding to non-radiative transitions.

Dr. F. E. Williams: The chemical deposition method of preparing transparent, non-scattering cathodoluminescent solids was discovered and developed by Studer and others.[10] The phosphor is prepared by reacting suitable vapours at the surface to be coated. Most of the ZnS phosphors have been prepared by evaporation of zinc and suitable activators in a H_2S atmosphere. Although the luminescence efficiency is less than that of powdered phosphors, because of internal trapping of the emission, the extraordinary contrast and resolution of the transparent screen renders it particularly suitable for applications where these properties are important.

Dr. E. Grillot: Zinc and zinc–cadmium sulphides have a stable cathodoluminescence. Pure CdS.Ag has a stable red fluorescence to ultra-violet or X-ray excitation,[11] but under cathode-ray excitation the initially bright emission disappears completely in some 10 seconds. This would seem to be of theoretical interest.

Dr. G. Günther: With reference to the sensitization of certain phosphate glasses by X-rays or γ-rays to give emission under ultra-violet excitation, is it possible to use the sensitization of fluoride phosphors by electron bombardment in a similar way to measure X-ray or γ-ray dosage quantitatively?

Author's reply: In reply to Dr. Bril, the influence of screen textures on the effective back scattering is mentioned in the paper. One would like to see some measurements of the magnitude of the back scattering of practical screens. In some cases the effect may be considerable, for example, when the phosphor crystal habit is mainly one of flat plates.

Dr. Klasens' contribution exposes a widely held misconception concerning the quantum efficiencies of sulphide

phosphors under long wavelength ultra-violet excitation. Again, more measurements on well-defined phosphors are required, in particular of the variation of quantum efficiency through the spectrum.

Dr. Fonda's suggestion that electron burn is due to ionic displacements seems improbable on energetic grounds. Very rapid electron burning can be produced by very slow electrons. The creation of competing centres by electron capture at suitable sites already present in the lattice appears to be a more probable mechanism.

In reply to Dr. Günther, the effect observed with fluoride phosphors under electron bombardment seems to occur only very slowly when these materials are subjected to X-rays or γ-rays.

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Paper 2

Preparation and characteristics of calcium halophosphates

By M. Doherty and W. Harrison, B.Sc., Siemens Lamp Research Laboratories, Preston

After a brief survey of the characteristics of the important antimony/manganese activated calcium halophosphates, a more detailed description is given of the dry and wet syntheses. The colour characteristics and the theoretical and attained efficiencies are discussed with reference to three halophosphates, the light blue, the daylight and the warm white. Maintenance of light output of fluorescent lamps, and the improvement of lamp colour by admixture with other phosphors, are also considered.

Mention of the activation of the calcium phosphate matrix was made as early as 1938,[1] although previously it had been observed that the mineral apatite which has an identical structure to the calcium halophosphate, $3Ca_3(PO_4)_2CaX_2$, where X = Cl or F, was sometimes weakly responsive to short wave ultra-violet radiation.[2] Calcium halophosphates were not themselves developed as phosphors until 1942.[3] It was then found that they belong to a class of phosphors which can be activated either singly by antimony or doubly by antimony and manganese much as calcium silicate can be activated by lead alone or lead plus manganese.

When the calcium halophosphate is activated by antimony alone the emission has a principal band in the visible spectrum peaking at approximately 4800 Å. The inclusion of manganese depresses the blue band and produces a second principal band with a peak at approximately 5850 Å. The manganese content and to a lesser degree the fluoride : chloride ratio can be varied to produce a range of phosphors giving near-white colours from light blue to orange; or in terms of fluorescent lamp colours, light blue, colour matching white, daylight and warm white can be prepared with a single halophosphate in each case. Whilst this is an attractive feature of the halophosphates it is probably less valuable than the two attributes of high efficiency and excellent maintenance characteristics which make the halophosphates the principal lamp phosphors to-day. The relative ease of preparation and the low cost of the halophosphates also make them attractive to the lamp maker.

PREPARATION OF CALCIUM HALOPHOSPHATES

The basic process

Two main stages are involved. The first is the preparation of a calcium phosphate of suitable purity and physical condition.

The phosphate may be either in the form of the pyrophosphate $Ca_2P_2O_7$; the tricalcium orthophosphate $Ca_3(PO_4)_2$, referred to below as the orthophosphate; or the calcium hydrogen orthophosphate $CaHPO_4$, referred to as the hydrogen phosphate.

The second stage is essentially a thermal treatment in which the calcium phosphate after intimate mixture with suitable compounds of activators and halogens is fired in an inert atmosphere at a temperature of 1050–1200° C.

Chemical and physical requirements for phosphor raw materials

The high degree of purity required is well appreciated. Thus, Leverenz[4] pointed out the importance of chemical purity and also of correct processing and of the final physical condition of the phosphor. He described luminescent purity as that where the impurity is less than 1 part per million. This degree of purity is perhaps higher than can be achieved in commercial manufacture, and fortunately another good feature of the halophosphates is that a higher impurity content can be tolerated than in some other phosphors, e.g. zinc beryllium silicate. It is of interest that chemical manufacturers in this country are responding to the demands

for phosphor quality chemicals and more information is becoming available on the purity of their products.

The particle size of the raw materials is an important factor; a small size is invariably desirable to achieve a finished phosphor of uniform composition and of suitable particle size without excessive grinding. The activators are added in small amounts only and it is particularly important that they be added in a state of subdivision which will give complete coverage of the calcium phosphate. A typical specification for one of the principal raw materials, calcium carbonate, is as follows:

Cu < 2 p.p.m.
Fe, Co, Ni, Pb, each < 5 p.p.m.
Cl, SiO_2, Na and alkali, each $< 0{\cdot}02\%$.
Mg $< 0{\cdot}03\%$.
Particle size approximately 5 μ.

Preparation of calcium phosphate

The dry synthesis. The calcium phosphate base may be either the pyro-, ortho- or hydrogen phosphate. In the phosphor laboratories with which the authors are associated a dry synthesis method was developed in 1945 and has been used on the commercial scale.[5] The starting materials are calcium carbonate and ammonium phosphate which are first ball milled together for intimate mixture and subsequently ignited. According to the calcium : phosphorus ratio in the starting materials either the pyro- or the orthophosphate should be formed according to the following reactions:

(*a*) pyrophosphate

$$2\,CaCO_3 + 2(NH_4)_2HPO_4 \xrightarrow{960^\circ C} Ca_2P_2O_7 + 4\,NH_3 + 2\,CO_2 + 3\,H_2O$$

(*b*) orthophosphate

$$3\,CaCO_3 + 2\,(NH_4)_2HPO_4 \xrightarrow{1100^\circ C} Ca_3(PO_4)_2 + 4\,NH_3 + 3\,CO_2 + 3\,H_2O$$

In practice the pyrophosphate can be obtained almost free from the orthophosphate, but in the preparation of orthophosphate some pyrophosphate and intermediate compounds tend to be formed.

A typical analysis of the pyrophosphate preparation showed that the theoretical calcium : phosphorus ratio was substantially achieved (Ca 31·5%, P_2O_5 55·9%), whilst analysis of the orthophosphate preparation gave a Ca content of 38% and a P_2O_5 content of 48% (theoretical values 38·7 and 45·8% respectively).

Photomicrographs of these phosphates are shown in Fig. 1.

The wet synthesis. Considerable study has been devoted to the precipitation of a consistent calcium phosphate and in 1938 the work of Hodge, Le Fevre and Bale[6] indicated that the most constant precipitate was the secondary phosphate, $CaHPO_4$. Since that time MacIntire, Palmer and Marshall[7] have suggested a method of preparing the tertiary calcium phosphate or tri-calcium orthophosphate $Ca_3(PO_4)_2$, but because of the protracted processing involved it is unsuitable for bulk production.

An alternative suggested method of preparing the orthophosphate is to neutralize a solution of orthophosphoric acid with calcium carbonate.[3] The authors have found that it is difficult to obtain consistent results with this method, the precipitate not being always of constant composition, and for bulk production the method tends to be rather laborious.

A method found to be satisfactory for the preparation of the hydrogen phosphate is precipitation from a solution of calcium chloride by di-ammonium hydrogen phosphate solution, added under controlled conditions.

To illustrate the procedure followed in the laboratory preparation, details are given as follows:

877 grams of A.R. calcium chloride ($CaCl_2 . 6\,H_2O$) were dissolved in 1 litre of distilled water and heated to 85° C. A second solution containing the phosphate radical was prepared by dissolving 530 grams of A.R. ammonium phosphate $(NH_4)_2HPO_4$ in 1·74 litres of distilled water and heated to 65° C. A partial precipitation was carried out by adding 10 ml. of ammonium phosphate solution to the calcium chloride solution and *vice versa*. In the final preparation the ammonium phosphate was passed at a constant rate into the calcium chloride and the combined solutions were vigorously agitated. The precipitate was finally washed until free from chloride.

A consistent yield of 97% calcium hydrogen phosphate of purity 99·99% has been obtained. A photomicrograph is also shown in Fig. 1. It will be noted that the particle size is smaller than that of the phosphates from the dry synthesis.

It is known to be important that all calcium phosphates and intermediates should be in the anhydrous state; otherwise hydroxyl ions partially replace the halide ions forming fluorescent calcium hydroxy phosphates which are unstable in low pressure mercury vapour lamps.

Activators

Antimony. Antimony is the primary or sensitizing activator, and is usually added to the intermediate compounds as trioxide. For optimum phosphor brightness the antimony content should be about 1·8% Sb by weight of the basic raw materials, but Butler, Bergin and Hannaford[8] have shown that only a trace of antimony induces the fluorescence, the remainder being either volatilized as antimony chloride or remaining as inert compounds. Butler and Jerome[9] have suggested that the antimony is present in the phosphor in the trivalent state.

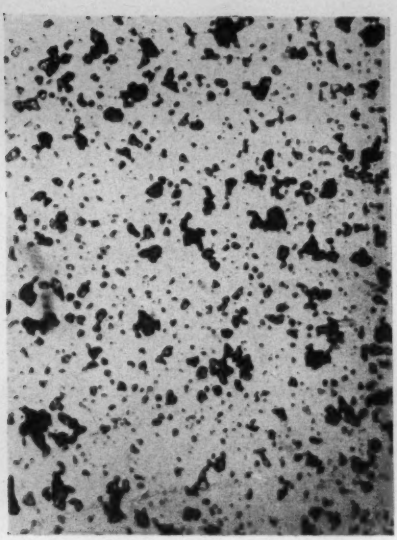
Manganese. Manganese is the secondary or colour modifying activator in the important antimony/manganese phosphor. The amount of manganese used may in practice be as high as 5%. The colour of the luminescence is a function of the manganese content, as discussed below.

Manganese is usually introduced as manganous carbonate or manganous phosphate. Both compounds produce efficient phosphors, but manganous carbonate is preferable as it does not introduce additional phosphorus to upset the balance of phosphorus to Ca + Mn.

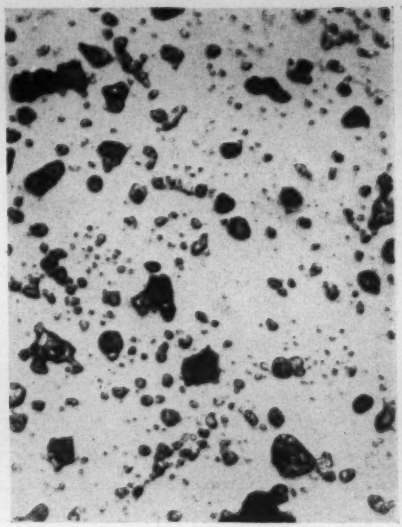
Butler and Jerome[9] have shown that the manganese is present in the divalent state. Extreme care must therefore be taken to ensure that the heat-treatment is carried out in a non-oxidizing atmosphere. Oxidation of the phosphor is indicated by a pink coloration and this is usually associated with inferior brightness when the phosphor is exposed to 2537 Å radiation; if, however, the oxidized layer is only superficial it can be removed by treatment with dilute hydrochloric acid.

Other activators. Other activators have been suggested to replace antimony. These include arsenic, lead, tin and bismuth as reported by Jenkins, McKeag and Ranby[10] and also silver reported by Ranby.[11]

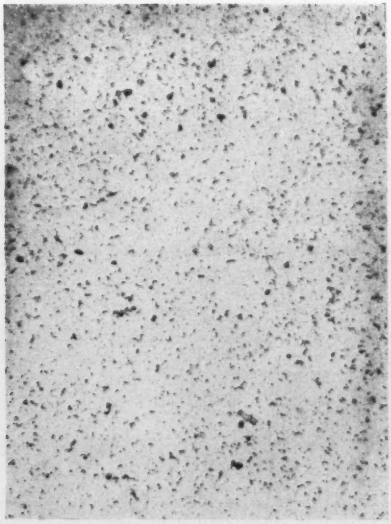
Phosphors employing these activators are, however, of considerably lower efficiency than the antimony/manganese



(*a*)



(*b*)



(*c*)

Fig. 1. Photomicrographs (×130) of calcium phosphates

(*a*) Orthophosphate. (*b*) Pyrophosphate. (*c*) Hydrogen phosphate.

phosphors and do not appear to have had commercial application.

Halides

The essential halide components of the matrix are introduced as the chloride or fluoride of calcium, strontium or ammonium. Calcium fluoride is predominantly used for the fluoride component because of its ease of preparation in the pure state and its reproducibility. The chloride radical may be introduced in the form of strontium, calcium or ammonium chloride. In practice strontium chloride is preferred, for calcium chloride is deliquescent and ammonium chloride increases the undesirable gaseous products in the firing reaction. When strontium is used it partially replaces calcium and due allowance has to be made for this in the ratio Ca + Mn : P. A moderate proportion of strontium has no significant effect on the phosphor characteristics.

Examples of commercial phosphors

In Table 1 are examples of halophosphate formulations. All contain antimony as the primary activator, but in the light blue the manganese content is nil, in the warm white it approaches the maximum, while the daylight is intermediate in composition.

Table 1. *Calcium halophosphate formulae (in gram atoms of raw materials)*

	Light blue	*Daylight*	*Warm white*
Ca	4·80	4·68	4·59
P	3·00	3·00	3·00
Sr	0·120	0·120	0·120
Mn	—	0·088	0·196
Sb	0·048	0·076	0·076
F	0·86	0·86	0·86
Cl	0·24	0·24	0·24

A satisfactory Ca : P ratio can be obtained with the addition of the necessary calcium fluoride only when the orthophosphate is used as a base, but with the pyrophosphate and the hydrogen phosphate additional calcium is required and is added in the form of calcium carbonate.

PROPERTIES OF CALCIUM HALOPHOSPHATES

Colour

Colour range with antimony and manganese activation. The range of spectral distribution obtainable with antimony and manganese activation of calcium halophosphate has been investigated by a number of workers. Nagy, Wollentin and Lui[12] have shown that as the manganese content is increased from zero to 5% a transition occurs from the single antimony band having a peak at 4800 Å to a doubly peaked distribution in which the manganese band, with its peak at about 5800 Å, eventually becomes predominant. They also showed that the peak of the manganese band could be shifted from 5800 to 5550 Å when the halogen was changed from all chlorine to all fluorine.

Butler and Jerome[9] have also investigated the emission spectra of the antimony/manganese calcium halophosphates. They examined 45 phosphors and found the emission induced by antimony to consist of a major band having a peak at 4870 Å and a minor band with a peak at 3960 Å; these bands were invariable in position, but their relative intensities varied according to the fluoride : chloride ratio. They found the manganese emission to consist of a major band having a peak between 5700 and 5950 Å according to the halogen ratio, and a minor band of about one quarter the intensity with a peak between 6250 and 6550 Å according to the halogen ratio. A low intensity band beyond 6700 Å was also suspected.

Fig. 2 shows the spectral energy distribution curves obtained for light blue, daylight and warm white phosphors as described

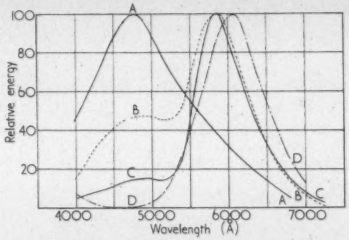


Fig. 2. Spectral energy distributions of calcium halophosphates and calcium silicate

A, Light blue; *B*, Daylight; *C*, Warm white; *D*, Calcium silicate. Pb, Mn.

in the preceding section. These have been adjusted to a maximum value of 100 in each case. To obtain a comparison of actual energies the warm white phosphor ordinates should be increased by about 1·3 times. To a first approximation the antimony emission may be regarded as a single wide band with a peak at approximately 4800 Å with a band width at half peak intensity of about 1500 Å. The manganese band may similarly be regarded as a single band having a peak at approximately 5850 Å, and 750 Å wide at half peak intensity.

In the warm white phosphor the antimony band intensity is depressed to about one-fifth of that in the light blue phosphor. The wide range of colours intermediate between the two is obtained simply by variation of manganese content, when changes in the proportions of antimony and manganese emission bands result. The fact that the positions of the bands in the spectrum and their widths are largely unchanged by variation of antimony, manganese and halogen content imposes a serious limitation on the spectral energy distributions possible with this class of phosphor.

In particular, the halophosphates are deficient in red emission. This can only be remedied if the band now provided by manganese activation is either shifted towards the red so as to have a peak above 6000 Å, or considerably broadened. So far there is no evidence that such improvements are possible.

The calcium silicate spectral distribution has been included in Fig. 2 as it has a band in the visible spectrum somewhat similar to the halophosphate manganese band but displaced about 250 Å towards the red. Like the antimony and manganese-activated halophosphate the lead and manganese-activated calcium silicate has two emission bands, but the band due to lead has a peak in the long wave ultra-violet region.

Fig. 3 is a section of the C.I.E. chromaticity diagram showing the chromaticities of the halophosphate lamps and also of the phosphors. The large shift from phosphor to lamp for the warm white and daylight phosphors is mainly due to the predominance of the 4358 Å line in the low pressure mercury discharge.

The line joining the light blue and the warm white lamp

co-ordinates and passing through the daylight point may be regarded as a locus of the manganese variable. It is interesting to note that it takes the form of a curve, whereas mixtures of actual light blue and warm white phosphors would give lamps lying on the straight line joining the appropriate chromaticity

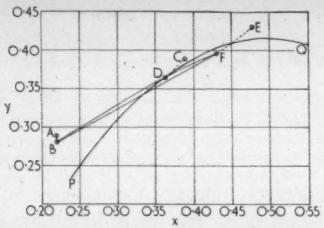


Fig. 3. Section of C.I.E. chromaticity diagram showing area for calcium halophosphates

A, Light blue phosphor; *B*, Light blue lamp; *C*, Daylight phosphor; *D*, Daylight lamp; *E*, Warm white phosphor; *F*, Warm white lamp; *BDF*, locus for single phosphor lamps; *BF*, locus for lamps with mixtures of *A* and *E*; *PQ*, Full radiator locus.

points. This indicates that a lamp made from a single halophosphate intermediate between light blue and warm white is slightly greener in colour than one made from a mixture of the two phosphors.

Fig. 4 (after Butler and Jerome[9]) shows the approximate area of the chromaticity diagram in which calcium halophosphates can lie; in this case phosphors are considered, not lamps. Here again it will be noticed that the loci of manganese variation take the form of curves, and inter-

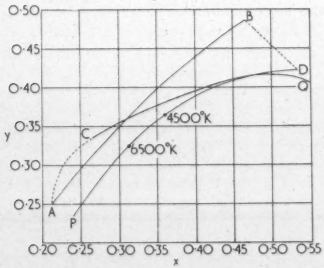


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Fig. 4. Section of C.I.E. chromaticity diagram showing area for calcium halophosphate phosphors. (After Butler and Jerome[9])

AB, Mn variation, 100% F; *CD*, Mn variation, 100% Cl; *AC*, F: Cl variation, no Mn; *BD*, F: Cl variation, Mn: P = 0·40 : 3 atoms; *PQ*, Full radiator locus.

mediate compositions will in general be slightly greener than the nearest equivalent mixtures of the extreme members of a series.

Luminous efficiency and maintenance

Factors affecting efficiency. Not all the chromaticities within the area shown in Fig. 4 can be achieved with a satisfactory luminous efficiency. The investigations of Nagy, Wollentin and Lui[12] into the chloride : fluoride ratio indicated that both 100% chloride and 100% fluoride, especially the latter, give lower luminance than mixtures of the halides, and that ratios of 2 : 1 or 1 : 2 are near the optimum. Of course the chromaticity has to be considered in the choice of the chloride : fluoride ratio and it is not always possible to design to the maximum efficiency.

The Ca + Sr + Mn : P ratio also affects the efficiency of the phosphor. The theoretical ratio derived from the apatite formula is 5 : 3, but it has been stated that the practical range has its optimum at 4·9 : 3 and that even slight deviation from this ratio results in an appreciable loss of efficiency.[13]

It is to be expected that the pyro-, ortho- and hydrogen phosphates will produce phosphors of similar efficiencies for the same atom ratio of Ca : P. In the authors' experience, however, the pyro- and hydrogen phosphates have given efficiencies about 5% higher than the orthophosphate.

In this country the declared efficiencies for halophosphate lamps have been increased by some 20% since their introduction in 1946. The improvement has resulted from improved raw materials and processing techniques and perhaps also from attention to the Ca + Sr + Mn : P ratio.

There are a number of factors in the lamp making process which must be carefully controlled to avoid undue depreciation of the phosphor efficiency. These include the milling processes in the lamp coating slurry preparation, the thickness of the coating, and the firing of the nitrocellulose binder, to mention only three.

Quantum efficiency. The quantum efficiency, or the ratio of the number of emitted quanta to the number of absorbed quanta, can obviously vary with the wavelength of the incident radiation and for phosphors in tubular fluorescent lamps it is necessary to have as high a response as possible to 2537 Å radiation. Nagy, Wollentin and Lui[12] gave excitation curves showing that halophosphates have near peak excitation at this wavelength, but at 1800 Å and over 3000 Å the excitation is low.

Values for the theoretical quantum efficiencies of halophosphate phosphors in fluorescent lamps are given as between 0·8 and 0·9.[14,15] The precise value is uncertain hence the calculation of the theoretical light output and efficiency of a fluorescent lamp is only approximate.[14,15]

Theoretical and attained efficiencies. A typical calculation of the distribution of energy for the 5 ft 80 W lamp follows.

The power loss in the cathodes may be determined from a consideration of the lamp volts of lamps of various lengths employing the same cathode from which the volt drop in the arc of the 5 ft lamp is calculated to be 93 V. The lamp volts are 106 at a current of 0·85 A; thus the volt drop in the two cathodes is 13, and the power loss 11 W.

The heat component of the discharge depends on operating conditions, but the authors' work indicates it to be approximately 18 W.

The energy distributed in the spectrum is the remaining 51 W:

5791 } 5770 }	5461	4358	4047	4000 to 3000	2537	1850 Å
0·2	0·6	0·9	0·5	1·8	40	7 W

The 2·2 W radiated in the visible spectrum contributes approximately 530 lumens to the total light output of the lamp.

The next step is to consider the conversion of energy from 2537 Å and 1850 Å to the spectral distributions of Fig. 2. Assuming a quantum efficiency of 0·8 the theoretical values of phosphor lumens of Table 2 are obtained. Adding 530 lumens due to mercury radiation, it follows that the theoretical efficiencies for 5 ft 80 W lamps are 60 lm/W for

Table 2. *Comparison of theoretical and attained efficiencies of phosphors in a 5 ft 80 W lamp*

Colour	*Conversion factor, (lm/W)**	*Conversion factor, 2537 Å to visible region*	*Theoretical value for phosphor (lumens)†*	*Lamp efficiency (lm/W)*	*Attained Value for phosphor (lumens)*	*Ratio of phosphor lumens attained to theoretical value*
Light blue	230	0·51	4230	45	3070	73%
Daylight	335	0·46	5600	60	4270	76%
Warm white	375	0·44	5940	64	4590	77%

Quantum efficiency taken as 0·8. * Value for 5550 Å = 680 lm/W.

† 40 W at 2537 Å + 7 W at 1850 Å taken as equivalent to 45 W at 2537 Å.

the light blue, 77 lm/W for daylight and 81 lm/W for warm white phosphors. If the quantum efficiency were increased to 0·9 these efficiencies would be increased by approximately 12%. The attained efficiencies given are approximate maxima achieved at the present time for 5 ft 80 W lamps at 0 hours.

When the daylight halophosphate lamp was introduced in 1946 the efficiency after 100 hours burning was 45 lm/W. By 1953 the corresponding value had been increased to 53 lm/W and efficiencies of the order of 60 lm/W have been achieved experimentally. Elenbaas[14] has expressed the view that an efficiency of 70 lm/W is possible.

Maintenance of lamp efficiency through life. The introduction of the halophosphate in 1946 gave improvements both in the 100 hours efficiency and in the maintenance of efficiency of fluorescent lamps through their life.

Fig. 5 shows the efficiency curves for the pre-1946 80 W daylight lamp (e.g. cadmium chlorophosphate + magnesium tungstate or zinc beryllium silicate + magnesium tungstate phosphor), and for the halophosphate in 1946 and 1953.

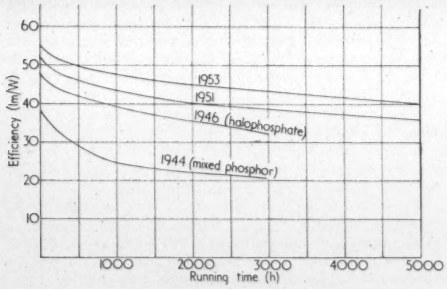

Fig. 5. Curves of efficiency through life of 80 W daylight fluorescent lamps

It may be noted that while the 1953 curve shows the 2000 hours efficiency as 85% of the 100 hours efficiency, claims have been made in the U.S.A. that values in excess of 90% can be obtained with "stabilized" phosphors; but these claims refer to the 4 ft 40 W lamp.

Froelich[16] has shown that phosphor depreciation in the fluorescent lamp is due to a photochemical reaction between excited mercury and the phosphor. Lowry[17] has suggested a three-fold deterioration from (*a*) mercury wetting a poorly reacted phosphor, (*b*) sodium contamination from the glass, (*c*) 1850 Å radiation acting on the active centres. Although these investigations were on the zinc beryllium silicate/magnesium tungstate phosphor the findings undoubtedly apply also to the halophosphates. A good maintenance characteristic is achieved when a phosphor has high chemical stability and added protection is given by coating it with a substance transparent to 2537 Å, but opaque to 1850 Å radiation, for example, antimony trioxide.

ADMIXTURE WITH OTHER PHOSPHORS

The excellent qualities of efficiency and maintenance and the low cost make it a safe rule that wherever possible halophosphates should be used in fluorescent lamps. However, if desired, they can be admixed with other phosphors to obtain intermediate efficiencies and colours. The most obvious case for an admixture of phosphors is to improve the red emission from the lamp. Two phosphors which technically are almost ideal for supplementing the halophosphate are magnesium germanate and magnesium arsenate, which have emission in a series of narrow bands principally between 6500 and 6600 Å, and which show good quantum efficiency and good maintenance. The combination of magnesium arsenate with halophosphates has been described by Ouweltjes.[18]

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DISCUSSION

Dr. G. R. Fonda: My measurements of quantum efficiency in terms of the ratio of quanta emitted to quanta absorbed are higher than those reported by the authors. I found about 85% for a phosphor containing optimum amounts of manganese and antimony, and 90–96% for a phosphor with antimony alone.

Mr. C. G. A. Hill: It is generally considered that a complete range of solid solution exists between fluoroapatite and chloroapatite. To examine this point and to study the influence of the halogen ratio on the position of the manganese emission, small single crystals of the apatites were grown from melts of calcium fluoride–chloride mixtures. X-ray examination of these crystals suggested strongly that while some solid solution occurred at the end of each range there was not a continuous series. Fluoroapatite crystals having values of the lattice parameter a from 9·39 to 9·47 Å and chloroapatite crystals having a values from 9·57 to 9·63 Å were found, but none of either structure between 9·47 and 9·57 Å.

When activated by manganese these crystals fluoresced under cathode-ray excitation. The emission peak of the 100% fluoroapatite was in approximately the same position as in the normal fluoroapatite phosphor. In the case of the 100% chloroapatite the peak occurred at a slightly shorter wavelength, and only the crystals with mixed halides showed emission at longer wavelengths.

Dr. J. L. Ouweltjes: Bodó[1] has determined the absorption coefficient of 2537 Å radiation for halophosphates. For a phosphor with 0·9% Sb and 0·5% Mn he found a value of 300 cm^{-1}. In commercial lamps the coating thickness is about 10 μ and so, neglecting the increase of optical path due to the granular structure, this would imply that about 75% of the 2537 Å radiation is transmitted by the phosphor and lost in the glass envelope. For 99% absorption a coefficient of 5000 cm^{-1} is required. Due to scattering in the powder this value may be reduced, but the discrepancy from the value obtained by Bodó seems too great to be explained in any simple way. Bodó's value is probably too low for commercial phosphors, but it seems certain that the absorption coefficient is much smaller than that for the zinc beryllium silicates. Thayer[2] has stated that the quantity of powder required to obtain maximum efficiency in a lamp is proportional to the particle size. We have explained this[3] by complete absorption of the 2537 Å radiation in the separate particles. For the halophosphates this proportionality holds above a certain minimum particle size, but below this limit more powder is required to obtain maximum light output. For maximum output a heavier coating thickness is required for the halophosphates than for the silicates. Phosphors made with particle size comparable with that of the silicates have so far always given a loss in brightness.

Dr. E. Nagy: With regard to the comments of Dr. Ouweltjes, the measurements of absorption coefficients and practical experience of fluorescent lamp coatings are not at all contradictory. If we assume an overall absorption of 95% of the ultra-violet radiation in the phosphor the difference in the coefficients is a factor of 10. The fluorescent coating does not consist of a single layer of grains, which would give incomplete covering, but in the efficient cases of 3 to 5 layers of grains. The weight of the coating is determined by the few grains of greatest size, around which a large number of smaller grains may be accommodated, so that the number of reflecting surfaces may be very high. This means that a high proportion of the exciting radiation passes through the coating many times before ultimate absorption. There are still other optical effects which also prevent the loss of exciting radiation by absorption at the glass wall. First, the radiation does not strike the wall normally but on the average at a large angle of incidence. Second, the unequal size and irregular shape of the individual phosphor grains make total reflexion of the exciting radiation at the phosphor-wall interface a possibility. That the halophosphates have a smaller overall absorption in lamps than the silicates is agreed, as this is shown by measurement of the respective absorption coefficients.

Dr. G. Günther: We have tried at Lumalampan to correct the colour rendering of halophosphates in the red. We find it advantageous to use two red components simultaneously, one having an emission partly in the long ultra-violet and violet regions, and partly in the orange-red (calcium silicate with Pb and Mn), the other having a longer wavelength red emission (magnesium germanate with Mn). These two powders complement each other excellently in their red emission, and besides this the germanate can transform some of the long ultra-violet and violet emission into red emission.

Mr. E. G. Steward: In discussion Mr. Hill described experiments which suggested that there was no continuous solid solution range for calcium fluoroapatite: calcium chloroapatite mixtures. X-ray examination of powder form phosphors shows solid solution to exist over the whole composition range.[4] Figs. 1 and 2 show the variations in

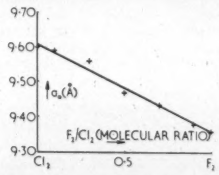

Fig. 1. Variation of a_0 dimension of hexagonal cell with molecular ratio F_2/Cl_2 in halophosphates

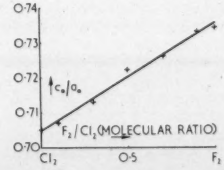

Fig. 2. Variation of c_0/a_0 ratio with F_2/Cl_2 ratio in halophosphates

cell dimensions with the molar ratio F_2/Cl_2. Within experimental limits the relations are linear, but further detailed work including chemical analysis is needed to check this. Similar X-ray results are given by Wallaeys and Chaudron,[5] and work by Nacken[6] indicates a linear relation with refractive index.

Author's reply: Dr. Fonda's experimental values for quantum efficiency of halophosphates indicate that our calculated theoretical phosphor lumens are on the conservative

side and the gap between theoretical and actual lumen achievement becomes a little greater than in Table 2.

Dr. Ouweltjes and Dr. Nagy discuss a matter of practical importance to the lamp maker, namely the transparency of the halophosphate to 2537 Å radiation with consequent effect on the weight of powder to be applied to a lamp, and also the important factors of particle size and distribution. It seems likely that near-optimum conditions of particle size and distribution and phosphor weight are now achieved in lamps and that the absorption of the 2537 Å radiation approaches the 95% mentioned by Dr. Nagy.

We agree with Dr. Günther that a mixture of calcium silicate and magnesium germanate is very suitable for addition to halophosphates to give improved colour rendering properties. Both phosphors have excellent maintenance characteristics.

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Paper 3

The investigation of new phosphors, with particular reference to the pyrophosphates

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There is a continuing demand for new phosphors in the fluorescent lamp industry and the initial stages of the search for suitable materials are essentially of a chemical nature. Some of the techniques used in this work are illustrated by reference to a large group of alkaline earth pyrophosphate phosphors recently developed. These materials utilize Sn^{2+} or Ce^{4+} as primary activator and manganese as secondary activator, and are of considerable potential application.

Physical methods of analysis have proved indispensable in providing an understanding of this pyrophosphate system. By means of X-ray and differential thermal analysis the various crystal structures of the pure pyrophosphates have been studied, and the conditions for the existence of the different forms established. Crystal data for the more important structures are given. The relationships between the main peaks of the emission bands, crystal structures and activators are discussed. A detailed study of such systems, in which interchange of matrix metal, well-defined crystal changes, and different activators produce marked changes in the fluorescence, may prove to be of importance in developing a useful theory of luminescence in activated inorganic solids.

Every year several new phosphor systems suitable for use in the conventional fluorescent lamp are discovered. However, very few of these materials attain any great importance in terms of the quantities eventually manufactured, mainly because of the high standards already achieved by existing materials. Nevertheless, the search for new phosphors continues, stimulated not only by the need for phosphors which are more efficient or cheaper to produce, but also by the possibility of discovering phosphors of new luminescence characteristics.

The discovery of new lamp phosphors is primarily a chemical operation involving the careful preparation of large numbers of potential phosphor samples for subsequent inspection under ultra-violet radiation. There are three main methods of approach in this search. The composition of an existing phosphor can be modified in the anticipation that the luminescent properties will be favourably changed, or chemical analogues of existing phosphors can be prepared and examined for luminescence, or materials for which no luminescence has been reported can be tested. When the last method of approach is used an appreciation of the physical properties which would be possessed by an "ideal" lamp phosphor is of much greater assistance than preconceived ideas regarding activators and impurity quenchers. In fact, the number of elements which can be investigated as possible activators is strictly limited, whereas the systems and conditions in which they can be tried are almost unlimited.

It is not uncommon in the search for new phosphors to find that the combination of a relatively well-established matrix and a known activator or activators is now luminescent, whereas all previous attempts to combine the two into a phosphor had proved unsuccessful. A phosphor of this type, which will be described in greater detail later, is calcium pyrophosphate activated by cerium and manganese. This combination was tried on previous occasions without success until, by a difference in approach, it was found to yield a very efficient phosphor. Such results justify occasional re-investigation of systems previously thought to be exhausted.

A class of phosphors extensively developed since 1950, which illustrates some of the techniques used in the search for new phosphors, is the alkaline earth pyrophosphate class. These materials show interesting relationships between chemical constitution, crystal structure and luminescence.

DEVELOPMENT OF THE PYROPHOSPHATE PHOSPHORS

Alkaline earth pyrophosphates have many of the properties considered desirable for the matrix of thermally prepared inorganic phosphors, but efficient materials of this type were at first largely restricted to cathode-ray excitation.[1,2,3]

One of the first known pyrophosphates appreciably excited by short-wave ultra-violet was the calcium salt activated by antimony and manganese[3]; more recently magnesium pyrophosphate with cerium, thorium and manganese has been described.[4] A phosphor which has shown that certain pyrophosphates are capable of achieving high luminescent efficiencies when used in discharge lamps, is barium pyrophosphate containing titania.[5] Historically, the latter material provided the starting point from which the pyrophosphates described below were developed.

All attempts to modify the colour of the luminescence of barium titanium phosphate either by incorporating secondary activators or by modifying the matrix proved unsuccessful except when the titanium is replaced by uranium. The latter material, however, has no advantage over the other uranium-activated barium phosphates.[6] Fluorescent barium titanium phosphate was obtained only when the temperature of preparation exceeded about 800° C. Differential thermal analysis on the matrix showed a sharp endothermic change near this temperature,[5] and subsequent X-ray analysis confirmed that a crystal change was involved. A re-examination of barium phosphate containing traces of possible activators, but prepared at temperatures well below the transition point, showed that activation by Sn^{2+} was possible to give a green phosphor, control of furnace atmosphere being required. Further investigation of the optimum firing conditions and tin concentration for this preparation then established that above about 800° C blue and red phosphors could be made.[7] Manganese could not be incorporated as a secondary activator for ultra-violet excitation.

The existence of these three forms of tin-activated barium pyrophosphate (and a fourth form with fluorescence of a cream colour) has been described independently.[8] From the published details, this cream form appears to approach the metaphosphate composition, and is not a pure pyrophosphate; a similar explanation may account for the blue form[7] which was made with a small excess of phosphorus pentoxide.

Attempts to prepare other alkaline earth materials corresponding to barium pyrophosphate (tin) phosphor showed that although the corresponding calcium compound is only weakly fluorescent, the strontium compound fluoresces bright blue and this also has been confirmed independently.[9] In contrast to the barium compound, strontium pyrophosphate can utilize manganese as a secondary activator with change in colour of the emission.[10] Moreover, the fluorescent colour of such materials containing a constant amount of manganese can be varied by replacing part of the strontium by other metals such as calcium or barium. Although the calcium compound is only weakly activated by tin or tin and manganese for ultra-violet excitation, calcium strontium pyrophosphates are as bright as the purely strontium compounds and give colours not found among the end members of the series.

Using a matrix of calcium strontium pyrophosphate and investigating other possible activators showed that cerium and manganese are effective in activating a yellow or pink fluorescence when the cerium is in the ceric state.[11] This is in contrast to other known alkaline earth metal phosphates activated by cerium and manganese in which it is necessary for the cerium to be in the cerous state. It was soon found that calcium pyrophosphate activated by Ce^{4+} and manganese is as brightly fluorescent as the calcium strontium material, a property in contrast to the activation by Sn^{2+} and manganese.

The main steps in the discovery of these phosphors may be summarized as follows:

$Ba_2P_2O_7.Ti$ } prepared in air

↓

3 forms (blue, green, red) ← $Ba_2P_2O_7.Sn$

↓

$Sr_2P_2O_7.Sn$ } prepared in controlled atmospheres

↓

$Sr_2P_2O_7.Sn, Mn$

↓

$CaSrP_2O_7.Sn, Mn$

↓

$CaSrP_2O_7.Ce, Mn$ } prepared in air

↓

$Ca_2P_2O_7.Ce, Mn$

From this field of phosphors it is the tin and manganese activated pyrophosphates of calcium, strontium and barium which will be described below.

PREPARATION OF TIN-ACTIVATED PYROPHOSPHATES

In the preparation of barium pyrophosphates activated by Sn^{2+} the ratio of barium oxide to phosphorus pentoxide in the matrix affects the fluorescent form obtained. A ratio of about $2BaO : 1{\cdot}08P_2O_5$ gives the red phosphor, but near $2BaO : 1{\cdot}25P_2O_5$ gives the blue phosphor. With tin-activated strontium pyrophosphate similar changes do not occur and although the fluorescence becomes very slightly more white in colour it is essentially blue for all compositions between $2SrO : 0{\cdot}98P_2O_5$ and $2SrO : 1{\cdot}3P_2O_5$, with an optimum ratio of about $2SrO : 1{\cdot}05P_2O_5$. A ratio of 2 moles alkaline earth metal oxide to 1·05 moles P_2O_5 was used in the preparation of the samples discussed below, except for activation by both tin and manganese, when the manganese was calculated as part of the 2 moles of alkaline earth oxide.

A convenient method of preparation of these phosphors is to heat the metal hydrogen orthophosphate ($MHPO_4$) obtained by precipitation, with any necessary addition of metal carbonate or ammonium phosphate to obtain the exact ratio of metal oxide to phosphorus pentoxide. Alternatively, mixtures of the calculated quantities of metal carbonate and an ammonium phosphate may be heated together. The matrix forming materials are heated with a tin compound either initially or after prefiring. If the tin is incorporated in the matrix as Sn^{4+} it is not effective as an activator for ultra-violet excitation. Stannous compounds tend to oxidize to the stannic state on heating in air with the pyrophosphate matrix forming materials. It is therefore necessary to control the atmosphere during the phosphor preparation to avoid oxidation of Sn^{2+} to Sn^{4+}. A somewhat cumbersome method which achieves this end is to heat the mixture first in air, then in hydrogen and again in air.[9] A much more simple and easily controlled method is to heat the matrix forming materials together with a stannous compound in an atmosphere of steam.[7,10] This prevents oxidation of the stannous compound, and the concentration of basic oxide is too low to give rise to hydroxyphosphates.

A suitable proportion of tin for activation is between 2 and 4% by weight of the matrix. The optimum temperature of heating depends on the matrix metal or metals and also on the proportions of activators.

GENERAL FLUORESCENCE CHARACTERISTICS

Tables 1, 2 and 3 illustrate the changes in fluorescence accompanying changes in composition of the calcium–strontium, strontium–barium and barium–calcium systems.

Table 1. *Fluorescence of calcium–strontium pyrophosphates*

Atoms of Mn per atom of P	Atomic ratio of Ca : Sr 100 : 0	95 : 5	75 : 25	50 : 50	25 : 75	5 : 95	0 : 100
0	W. blue	W. blue	W. blue	Blue	B. blue	B. blue	B. blue
0·024	W. yellow	Yellow	Pink	B. pink	Pale pink	Pale pink	Bluish-white
0·048	W. yellow	Yellow	B. orange	B. orange	Pink	Pink	Bluish-white
0·111	W. yellow	W. yellow	B. orange	B. orange (Fig. 2)	Pink	Pink	Pale pink

Table 2. *Fluorescence of strontium–barium pyrophosphates*

Atoms of Mn per atom of P	Atomic ratio of Sr : Ba 100 : 0	95 : 5	75 : 25	50 : 50	25 : 75	5 : 95	0 : 100
0	B. blue	B. blue	B. blue	Green-blue	B. green	W. red	W. red
0·024	Bluish-white	Bluish-white	Bluish-white	Greenish-white	Green	W. red	W. red
0·048	Bluish-white	Pale pink	Pale pink	Greenish-white	Green	W. red	W. red
0·111	Pale pink (Fig. 3)	Pale pink	Pale pink	Greenish-white (Fig. 4)	Green	W. red	W. red

Table 3. *Fluorescence of barium–calcium pyrophosphates*

Atoms of Mn per atom of P	Atomic ratio of Ba : Ca 100 : 0	95 : 5	75 : 25	50 : 50	25 : 75	5 : 95	0 : 100
0	W. red	W. red	Bluish-white	Greenish-white	B. pale blue	W. blue	W. blue
0·024	W. red	W. red	Pink	W. yellow	Pale pink	W. yellow	W. yellow
0·048	W. red	W. pink	W. orange	W. yellow	Pink	Yellow	W. yellow
0·111	W. red	W. pink	W. pink	W. orange (Fig. 5)	Orange	W. orange	W. yellow

W. = weak. B. = bright.

The fluorescence is that excited by predominantly 2537 Å radiation at room temperature. All the materials contain 0·05 atoms of tin per atom of phosphorus and the atomic ratio of alkaline earth metals plus manganese to phosphorus is constant at 1 : 1·05. The alkaline earth metals are expressed as an atomic ratio of one another. All the samples were prepared at 900° C.

X-ray and spectral emission measurements show that these complicated fluorescence changes are intimately associated with the crystal structure of the system.

CRYSTAL STRUCTURE OF PYROPHOSPHATES

X-ray diffraction studies of calcium pyrophosphate, prepared by heating secondary calcium phosphate, show that it exists in three different forms, depending on the temperature of firing. Two of these have been previously reported,[12] the α form occurring at temperatures above about 1150° C, and the β form existing at lower temperatures. In addition, a third modification, the γ form, has now been found to occur below 750° C.

Similarly strontium pyrophosphate is found to be dimorphic with a transition temperature of about 750° C. The high temperature or α form is isomorphous with α calcium pyrophosphate, and the β form prepared below 750° C is isomorphous with β calcium pyrophosphate. The existence of a third form at even lower temperatures is suspected.

Barium pyrophosphate also exhibits two modifications. Firing temperatures less than about 790° C yield a structure isomorphous with α $Ca_2P_2O_7$ and α $Sr_2P_2O_7$ and accordingly named α $Ba_2P_2O_7$. This accounts for the green $Ba_2P_2O_7$.Sn phosphor previously mentioned. At higher temperatures a new structure appears having no isomorph among the calcium and strontium compounds. This is now called δ $Ba_2P_2O_7$. This provisional nomenclature departs from the custom of naming α, β, . . . from the high temperature form downwards, but permits the isomorphous forms to be represented by the same prefix.

The system can be represented as follows:—

Calcium pyrophosphate $\gamma \xrightarrow{750^\circ\,C} \beta \xrightarrow{1150^\circ\,C} \alpha \longrightarrow$ m.p.

Strontium pyrophosphate $\beta \xrightarrow{750^\circ\,C} \alpha \longrightarrow$ m.p.

Barium pyrophosphate $\alpha \xrightarrow{790^\circ\,C} \delta \longrightarrow$ m.p.

Isomorphous forms occur diagonally as indicated in the preceding paragraphs.

Interplanar spacings of these structures obtained from X-ray diffraction photographs are given in Table 4 together with line-intensities of the patterns. The complexity of the patterns makes them difficult to index. Single crystals of α $Ca_2P_2O_7$ and α $Sr_2P_2O_7$ large enough to manipulate have been produced by controlled cooling of the melt, and from their diffraction patterns the unit cell symmetry and dimensions have been calculated. The α forms are orthorhombic, with the following lattice parameters:

	a	b	c
$Ca_2P_2O_7$	8·44	12·52	5·26 Å
$Sr_2P_2O_7$	8·87	13·27	5·39 Å
$Ba_2P_2O_7$	9·35	13·87	5·61 Å

(The $Ba_2P_2O_7$ pattern was indexed by analogy with the others.)

Sufficiently large crystals to determine the constants of the β, γ, and δ forms have not yet been obtained.

From the structural details given it is possible to throw light on the phosphor properties. Thus the δ or high temperature form of barium pyrophosphate has no isomorphs, and this individuality is reflected in its properties as a phosphor matrix. Its unique behaviour with titanium dioxide has

Table 4. *Interplanar spacings and relative line intensities in X-ray diffraction patterns of alkaline earth pyrophosphates*

α-$Ca_2P_2O_7$		β-$Ca_2P_2O_7$		γ-$Ca_2P_2O_7$		α-$Sr_2P_2O_7$		β-$Sr_2P_2O_7$		α-$Ba_2P_2O_7$		δ-$Ba_2P_2O_7$		*Barium titanium phosphate*
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	
7·04	vw	4·72	vw	4·47	w	7·34	m	4·86	m	3·56	vs	3·87	vs	
4·85	w	4·43	vw	3·33	s	6·61	w	3·45	s	3·26	s	3·48	m	Pattern as for
4·18	w	3·34	s	3·05	vs	3·41	vs	3·32	s	3·02	vw	3·06	vw	δ $Ba_2P_2O_7$ with
3·72	w	3·22	s	2·91	vs	3·31	m	3·19	m	2·81	s	2·80	s	addition of
3·49	w	3·09	m	2·67	m	3·18	m	3·09	vs	2·65	vw	2·69	s	following lines
3·26	s	3·01	vs	2·53	m	3·10	m	3·01	m	2·52	vw	2·30	s	*d* (Å) *I*
3·16	s	2·90	m	2·38	vw	2·88	m	2·88	md	2·30	s	2·25	m	2·77 vw
3·04	m	2·80	m	2·34	m	2·68	s	2·77	vw	2·13	s	2·21	m	2·65 w
2·74	m	2·75	m	2·21	s	2·54	m	2·65	md	1·94	s	2·14	s	2·37 w
2·63	m	2·68	w	2·16	m	2·39	m	2·44	m	1·78	vw	2·09	s	1·99 m
2·58	m	2·54	m	2·08	m	2·19	m	2·31	m	1·74	w	1·95	m	1·75 w
2·43	m	2·40	vw	1·94	vw	2·04	s	2·18	m	1·67	vw	1·86	vw	1·43 vw
2·40	m	2·33	m	1·85	md	1·97	m	2·16	m	1·64	vw	1·80	m	1·29 vvw
2·08	s	2·27	vw	1·80	m	1·86	m	2·06	m	1·49	w	1·76	w	
2·03	m	2·22	m	1·77	m	1·85	m	2·02	m	1·46	w	1·71	vw	
1·97	s	1·99	m	1·72	m	1·70	w	1·92	m	1·39	w	1·62	vw	
1·82	w	1·95	m	1·65	m	1·67	m	1·83	vw			1·58	m	
1·77	m	1·85	w	1·56	m	1·59	vw	1·79	vw			1·53	m	
1·70	vw	1·83	w	1·50	m	1·56	vw	1·67	md			1·48	m	
1·60	m	1·77	m	1·46	m	1·35	w					1·46	w	
1·57	vw	1·31	m	1·30	m	1·33	w					1·40	w	
1·29	m					1·24	w					1·39	vw	
1·24	w											1·35	m	
Index lines														
3·26		3·01		3·05		3·41		3·09		3·56		3·87		
1·97		3·34		2·91		2·04		3·45		1·94		2·80		
3·16		3·22		3·33		2·68		3·32		2·13		2·69		
2·08				2·21								2·14		

(vs = very strong, s = strong, m = medium, w = weak, vw = very weak, d = diffuse. Intensities estimated visually.) CuKα radiation, 11·46 cm diameter camera.

been mentioned. The diffraction pattern of barium titanium phosphate differs only slightly from that of δ $Ba_2P_2O_7$, having extra lines which are not due to a separate phase. Interplanar spacings are given in Table 4.

A further difference between the pure δ form and the phosphor is shown by the behaviour on prolonged grinding. The δ form does not lose its crystal identity and is merely reduced in particle size, but the phosphor appears to disintegrate into several products with unidentified diffraction patterns.

Considering now the isomorphous materials, these can form ranges of solid solutions changing slowly in unit cell size while retaining the α or β structures. Transition temperatures of the solid solutions are different from those of the pure substances, the relationship being shown approximately in Fig. 1. Differential thermal analysis was used as well as X-ray analysis in constructing this diagram. The relationships are important for the prediction of the type of fluorescence which will occur at any temperature and composition within the system. The diagram must be interpreted with caution since the presence of activators also appears to affect the transition temperatures considerably. Some regions of the system, modified by the presence of activators, have not yet been fully explored though sufficient has been done to establish the crystal changes shown in Fig. 6. Fuller details will be published elsewhere, but in the following a preliminary correlation is demonstrated between the X-ray results and the luminescence.

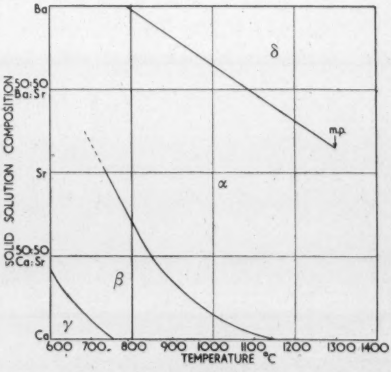


Fig. 1. Approximate phase diagram for pure pyrophosphates

SPECTRAL ENERGY DISTRIBUTION CURVES OF PYROPHOSPHATES

Samples of phosphors prepared as described above were packed into a small quartz cell and irradiated by a low-pressure mercury vapour discharge in a quartz envelope. The excitation, although mainly of 2537 Å radiation, included some 1850 and 3650 Å radiations. The spectral energy distribution (s.e.d.) curves were determined[13] and plotted on the basis of frequency against energy per unit frequency interval. The curves were analysed by trial and error into Gaussian distributions $I = I_0 \exp[-a(\nu - \nu_0)^2]$. Figs. 2–5* show the results for samples included in Tables 1 to 3: see references in these tables. The close fit to theoretical distributions is shown in simpler cases (Fig. 2).

In analysis of this kind it is often difficult to decide which component bands of the emission curves are genuine, especially when small residuals are found. Correlation in an extensive series such as the present one is helpful for deciding such questions. The results of s.e.d. measurements on some of the samples described in Tables 1, 2 and 3 (Mn 0·111) are summarized in Fig. 6, in which only the two most important peaks are plotted, together with indications of the crystal changes. Many of the long wavelength bands can be resolved to show weak components nearer the red end of the spectrum, but these determinations are not very precise and are ignored in the following discussion. The incomplete nature of Fig. 6 in regard to the number of peaks present, and their intensities, makes it difficult to deduce, from this figure, the colours given in Tables 1 to 3.

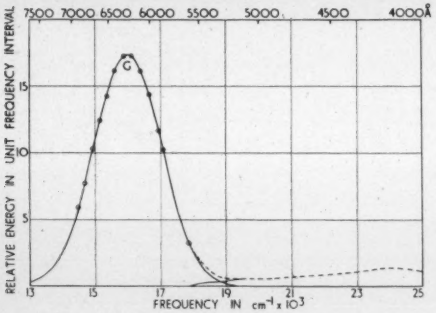
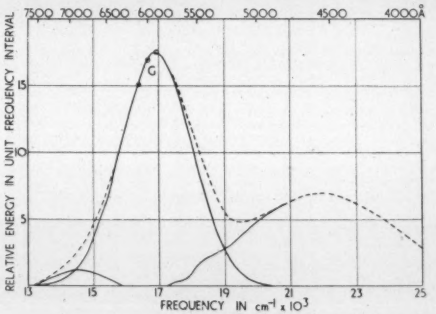

7500 7000 6500 6000 5500 5000 4500 4000Å
RELATIVE ENERGY IN UNIT FREQUENCY INTERVAL
G
13 15 17 19 21 23 25
FREQUENCY IN cm⁻¹ x 10³

Fig. 2. S.e.d. curve for $CaSrP_2O_7$.Sn, Mn (α form). Ca : Sr = 50 : 50 atoms. Sn 3·6%, Mn 4·3% by wt.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FREQUENCY IN cm⁻¹ x 10³

Fig. 3. S.e.d. curve for $Sr_2P_2O_7$.Sn, Mn (α form). Sn 3·6%, Mn 4·3% by wt.

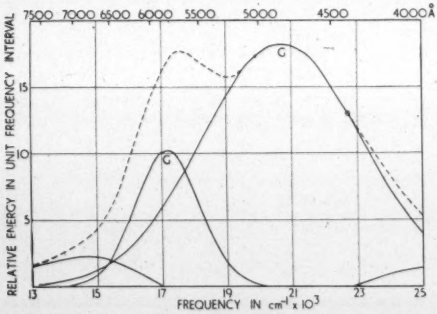
7500 7000 6500 6000 5500 5000 4500 4000Å
RELATIVE ENERGY IN UNIT FREQUENCY INTERVAL
G
G
13 15 17 19 21 23 25
FREQUENCY IN cm⁻¹ x 10³

Fig. 4. S.e.d. curve for $SrBaP_2O_7$.Sn, Mn (α form). Sr : Ba = 50:50 atoms. Sn 3·6%, Mn 6·4% by wt.

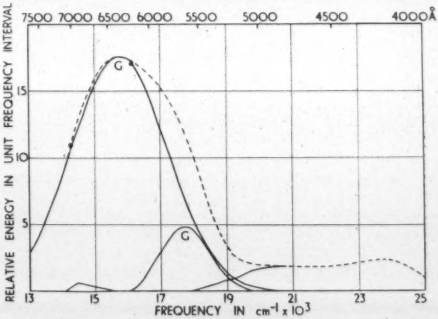
7500 7000 6500 6000 5500 5000 4500 4000Å
RELATIVE ENERGY IN UNIT FREQUENCY INTERVAL
G
G
13 15 17 19 21 23 25
FREQUENCY IN cm⁻¹ x 10³

Fig. 5. S.e.d. curve for $BaCaP_2O_7$.Sn, Mn (indefinite crystal form). Ba : Ca = 50 : 50 atoms. Sn 3·6%, Mn 5·0% by wt.

Figs. 2–5. Experimental curves shown by broken lines where these are not coincident with full lines
Full lines are Gaussian curves when marked *G*, otherwise they are residual differences between Gaussians and experimental curves.

* The wavelength scales in Figs. 2–6 are inserted merely to assist in visualizing the band positions. The peaks are to be read off from the frequency scale; they would be shifted slightly if the bands had originally been plotted on a wavelength scale.

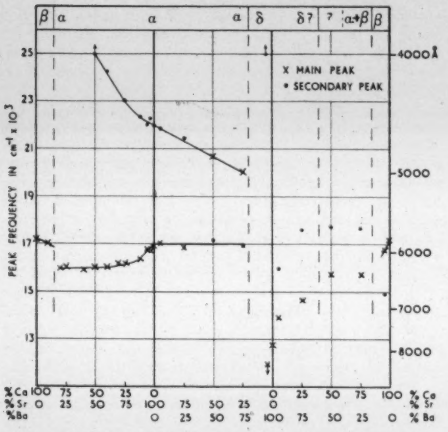

Fig. 6. Summarized results of analysis of s.e.d. curves for phosphors fired at 900° C, with corresponding X-ray structures. Atoms Mn/P = 0·111 throughout

Abscissae are atomic percentages.
Points marked with arrows indicate peaks beyond range of the instrument.

CRYSTAL FORM AND EMISSION FOR TIN ACTIVATION

Calcium strontium pyrophosphates activated by Sn^{2+} alone show little change in emission colour with crystal structure, both α and β forms fluorescing blue. This blue band due to Sn^{2+} is wide and the position of the main peak is not appreciably affected by varying the concentration of tin. With the incorporation of manganese new bands appear in the emission spectrum, and the fluorescence colour now depends closely on the crystal structure of the phosphor; in general α forms fluoresce orange or pink and β forms yellow (pyrophosphates activated with Ce^{4+} and manganese behave similarly, see below).

The secondary activation by manganese is a sensitization process. For example, the blue emission from α $CaSrP_2O_7$ is a wide band with a main peak at 21 870 cm^{-1}, but the incorporation of manganese reduces the intensity of this tin band and at the same time produces an emission with a peak at lower frequencies. See Table 5.

Table 5. *Sensitization effect in $CaSrP_2O_7$. Sn, Mn. Ca : Sr* = 50 : 50

Atoms of Mn per atom of P	*Mn band* ν_0 *in* cm^{-1}	*Intensity*	*Sn band* ν_0 *in* cm^{-1}	*Intensity*
0	17 130	3·8	21 870	56
0·024	16 700	70	21 930	32
0·048	16 300	100	22 750	13·5
0·111	16 100	83	—	—
0·159	15 700	87	—	—

Since the transition temperature for the crystal change depends on the concentration of activators and also on the ratio of calcium to strontium in the matrix, a series of phosphors prepared at a constant temperature (Table 1) will include both α and β forms. Hence the marked change in the position of the main peak of the calcium–strontium series at 80Ca : 20Sr (Fig. 6) where there is a transition from the β to the α form. In the main series of Ca–Sr–Ba it is interesting to note the approximate constancy of the main peak position and the rapid variation of the (blue-green) secondary. The rise of the latter to predominance at 50Sr : 50Ba is due to a rapid fall in the intensity of the orange band. Attempts are being made to correlate the small changes in the main peak position with changes in the lattice constants.

The orange band in the α Ca–Sr–Ba series has a constant in the Gaussian equation of $a \simeq 4$ to 6×10^{-7} cm^2, while the blue-green band has $a \simeq 1 \times 10^{-7}$ cm^2.

With barium pyrophosphate the position is somewhat different. Titanium efficiently activates the δ but not the α form; both forms are activated by Sn^{2+} with emission in the red (δ) or green (α). This contrasts with the corresponding calcium and strontium pyrophosphates which emit in the blue. Unlike the α forms of calcium and strontium pyrophosphate, neither α nor δ $Ba_2P_2O_7$ allows the incorporation of manganese as a secondary activator.

Because of these differences, series of calcium–barium and strontium–barium pyrophosphates activated by tin and manganese show fluorescent changes similar to the calcium–strontium system only when the proportion of barium is low. At higher proportions of barium the systems behave as if they were essentially barium pyrophosphate activated by tin alone, the calcium or strontium and manganese having little effect on the luminescence. In Fig. 6 increasing barium in the strontium–barium series leads to reversal of the relative importance of the main peaks and a complete change of character when the δ form appears at >80% Ba. The incomplete s.e.d. curve at 95% Ba, for instance, shows both bands to be largely outside the visible region, and this is also the case for red δ $Ba_2P_2O_7$.Sn mentioned above. The barium–calcium series is rather more complicated and the X-ray patterns do not show very clear transitions.

Since the samples used for these measurements have all been prepared at a constant temperature, the observed emission intensities do not necessarily indicate the intensities which could be achieved by each phosphor if prepared under the optimum conditions to yield a particular crystal form.

CERIUM AS AN ACTIVATOR

When the Sn^{2+} activator of calcium strontium pyrophosphate systems is replaced by Ce^{4+} the emission is almost entirely in the ultra-violet region for both α and β forms. When manganese is present as a secondary activator in the β form a yellow emission is observed; this becomes a pink emission in the α form (see Table 7). Because the emission band due to the cerium is in the ultra-violet region, phosphors containing small concentrations of manganese do not show the intermediate blue-white emission colours of the corresponding tin-activated materials. Increasing the manganese concentration in a given crystal form of the cerium-activated matrix merely affects the intensity of the yellow or pink emission.

DISCUSSION

The properties of these pyrophosphate phosphors are similar to those of the Sn^{2+}-activated alkaline earth orthophosphates,[14] in which the emission colour is determined solely by the crystal structure of the matrix and not by the concentration of tin. Manganese can be incorporated as a secondary activator in the orthophosphates and here also

the emission band due to tin is gradually suppressed and that due to manganese gradually increases with increasing manganese concentration.

Any comparison between the cerium and manganese-activated pyrophosphates and the similarly activated alkaline earth orthophosphates[15] is complicated by the differing valency states of the cerium.

From a consideration of ionic radii (see Table 6) it is not surprising that the calcium–strontium and strontium–barium pyrophosphate systems form solid solutions in which crystal changes correspond with emission changes but in the case of the extreme members in ionic size—calcium and barium—the system is more complicated.

Table 6. *Ionic radii (crystal radii)*[16]

Ion	*Ionic radius, Å*
Ca^{2+}	1·05
Sr^{2+}	1·18
Ba^{2+}	1·38
Mn^{2+}	0·83
Sn^{2+}	1·02
Ce^{4+}	1·01

In the pyrophosphates manganese presumably replaces divalent cations when introduced as an activator. An explanation for the non-activation of the barium pyrophosphates (and some other barium phosphors) by manganese may lie in the wide difference between the ionic radii of manganese and barium.

The almost identical ionic sizes of Ce^{4+} and Sn^{2+} correspond to an agreement in the positions of the main peak of the manganese emission bands when the latter element is present as a secondary activator (Table 7).

Table 7. *Frequency of peak of main emission band*

Matrix	*β form*		*α form*	
	Sn^{2+}	Ce^{4+}	Sn^{2+}	Ce^{4+}
$Ca_2P_2O_7$	17 450	17 450	16 400	16 200 cm^{-1}
$CaSrP_2O_7$			16 160	16 180
$Sr_2P_2O_7$			16 700	16 350

All preparations with 0·08 atoms Mn per atom P, and primary activator as shown.

It is unfortunate that the conditions required for the preparation of Sn^{2+} and Ce^{4+}-activated pyrophosphates exclude phosphors containing both activators together. However, the ionic sizes and electrochemical characters of Sn^{2+} and Ce^{4+} indicate that in activating proportions these ions can occupy positive ion sites in the pyrophosphate matrices.

A more detailed examination of systems such as that described might elucidate factors which are necessary for the successful activation of phosphors generally. This may also be of considerable importance in the development of any useful theory of inorganic luminescence, and though this approach seems somewhat obvious and empirical by comparison with the fashionable theoretical approach using wave mechanical methods, it is by no means certain that the latter will be the first to make valid predictions of new phosphors.

ACKNOWLEDGEMENT

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DISCUSSION

Mr. D. H. Mash: In the X-ray data of Papers 3 and 4 independent studies overlap. Comparison shows good agreement in the spacings for α $Ba_2P_2O_7$ (the low temperature form), but for δ $Ba_2P_2O_7$ agreement is only good for relative spacings, the values of McKeag and Steward being all about 1% higher than those in our paper. The same 1% difference occurs for α $Sr_2P_2O_7$. One reason for these differences may be that McKeag and Steward's powders contain 2% tin as impurity whereas ours were pure, but this is not expected to explain the whole of the difference.

It should be noted that this phosphor system offers better opportunities than any other known for studying the effect of varying lattice dimensions, crystal form, activators and chemical composition on luminescence, as all these factors can be varied over wide ranges without loss of fluorescent properties.

Mr. E. G. Steward: Mr. Mash has mentioned that the X-ray data for some of their compounds differ slightly from ours. This may be due to different activator concentrations in the two cases: our figures refer to phosphors containing 2% tin.

The barium titanium phosphate phosphor is described as having a pattern "as for δ $Ba_2P_2O_7$ with the addition of the following lines. . . ." Does this not suggest that the material contains more than one phase?

Dr. K. H. Butler: Paper 3 is a very interesting contribution to phosphor theory and technology. It shows clearly the effect of ionic size on crystal structure and phosphor behaviour.

A few differences have been found in our own work on this system:

(*a*) $\alpha\ Ca_2P_2O_7$ gave a pure blue emission with Sn^{2+}, while the β form gave some red emission as well as blue.

(*b*) The existence of $\beta\ Sr_2P_2O_7$ was confirmed but shown to be stable to 800° C or slightly above. The first five strong X-ray lines gave spacings of 4·89, 3·44, 3·32, 3·18 and 3·08 Å, in excellent agreement with the present paper. I agree with the comment that the empirical approach will be more profitable than the theoretical in predicting new phosphors.

Miss M. Doherty: (*a*) In calcium orthophosphate, magnesium pyrophosphate and other phosphors with cerium and manganese activation the cerium may be replaced by thallium. Have the authors found this in their calcium and calcium–strontium pyrophosphates?

(*b*) When cerium and thallium-activated phosphors are in contact with mercury vapour in the low-pressure discharge lamp we find deterioration of light output. Is this the case with these new pyrophosphates?

(*c*) Extreme care has apparently been taken to keep the tin in the stannous and the cerium in the ceric state. It has been stated that manganese replaces divalent cations. Has any difficulty been experienced in keeping the manganese in the divalent state during phosphor preparation, particularly since two different types of atmosphere are used?

Dr. F. A. Kröger: What is the evidence for Ce^{4+} as a luminescence centre in the pyrophosphates? The conclusion seems doubtful for two reasons:

(*a*) Ce^{4+} has lost the *f*-electron which causes the characteristic rare-earth properties of Ce.

(*b*) The ultra-violet emission found by the authors would be expected for Ce^{3+}.

Chemical analysis to prove the existence of Ce^{4+} is desirable.

Dr. H. A. Klasens: It cannot be concluded from the firing conditions alone which valency an activator ion has in the phosphor. The basic lattice is also of major importance in determining this valency. This is clearly demonstrated by the fact that manganese in magnesium arsenate is tetravalent but divalent in zinc silicate, although both phosphors are fired under identical conditions.

Authors' reply: In reply to Mr. Steward, the possibility of a second phase in the barium titanium phosphate phosphor was indeed an obvious explanation, but this has not been confirmed by further investigation. Repeated experiments have failed to alter the intensity of the extra lines with respect to those for $\delta\ Ba_2P_2O_7$. The disintegration on grinding, in contrast to the stability of $\delta\ Ba_2P_2O_7$, shows that considerable modification of the matrix has been caused by TiO_2, and it is suggested that a superlattice is formed.

In reply to Miss Doherty:

(*a*) Thallium or lead can be used in place of tin or cerium, but the brightness of the pyrophosphates is then poor compared with the materials described.

(*b*) Provided excess of cerium is avoided during the preparation, the pyrophosphates do not show excessive deterioration in fluorescent lamps.

(*c*) No difficulty has been experienced with manganese during firing, for, in contrast to other activators, manganese is often unaffected by the atmosphere.

In reply to Dr. Kröger and Dr. Klasens, the evidence for believing that the cerium activator is tetravalent is as follows:

(*a*) It is necessary to prepare these materials in air and not in the reducing atmosphere which is essential for activating the known alkaline earth orthophosphates by Ce^{3+}.

(*b*) The ionic radii of Sn^{2+} and Ce^{4+} are practically identical, whereas Ce^{3+} is appreciably larger and would not be expected to give the remarkably similar band positions shown in Table 7.

As is usual with phosphors, ordinary chemical analysis is not reliable for determining the valency of an activator because the matrix can often be dissolved only with difficulty, and there is no justification for believing that the valency of the activator ions when in solution is the same as in the original phosphor; the presence of secondary activators further complicates the problem. As suggested by Garlick, physical measurements are more promising for determining the valency of activators in phosphor matrices.

Paper 4

The luminescent properties and crystal structure of some new phosphor systems

By A. H. McKeag, M.Sc., A.R.I.C., and E. G. Steward, B.Sc., A.Inst.P., Research Laboratories, The General Electric Company, Ltd., Wembley, Middlesex

New phosphor systems are described which illustrate the importance of combining the study of fluorescent properties of new systems with the results of X-ray analysis. The systems described include a range of tin-activated pyro- and tetraphosphates of strontium and barium, and a group of manganese or cerium-manganese-activated silicates containing lithium. The preparation and fluorescent properties of these phosphors are discussed.

X-ray methods have been used to identify the phases responsible for the various phosphors and a number of new phases including polymorphic forms, have been found. X-ray powder diffraction data are included.

The practical importance of the new phosphors is discussed with reference to fluorescent lamps in general. Emphasis is placed on the colour correction of high pressure mercury vapour lamps by certain members of the complex lithium-containing silicate phosphors.

1. Introduction

In recent years X-rays have been widely used for the identification and specification of new phosphors.[1] As a result, the crystal structure and composition of most of the more important phosphors are well established. Frequently the identification of a new phosphor is straightforward because the matrix is based on a well-known compound or mineral. In other systems, however, the conditions of preparation which have been selected have led to the formation of a compound for which X-ray diffraction data have not previously been published, or to an entirely new material which has not previously been prepared. The recognition of new phases will then depend on the results of a study of the effect of changes in conditions of preparation on the fluorescent properties of the material, combined with an X-ray examination of the resulting phosphors. One of the earliest examples of this combined form of investigation was the discovery by Schleede and Gruhl,[2] of the polymorphism of zinc orthosilicate.

The present paper provides further illustration of the use of X-ray methods in phosphor development and deals with two new classes of luminescent materials: the luminescent properties and field of application of these new phosphors are also described.

The new phosphor systems consist of :

(i) A range of strontium and barium phosphates activated by tin alone or by tin and manganese, which are excited by short ultra-violet radiation.

(ii) A group of complex silicates containing lithium, activated by manganese or by cerium and manganese, which are excited by short ultra-violet radiation and also in some instances by long ultra-violet radiation.

The variations in fluorescent properties of these two groups with changes in composition and conditions of preparation have been examined. X-ray examination of the products has led to the identification of the separate phases responsible for the fluorescent properties. It will be evident from these examples that the fluorescent properties, combined with X-ray examination, may provide a useful technique for studying phase changes in a given system if suitable activating conditions for the materials can be found.

2. Structure and luminescent properties of strontium and barium phosphates activated by tin

Tin-activated strontium and barium pyrophosphates and tetraphosphates are described in this paper; these provide a wide range of emission bands throughout the visible spectrum.[3] Kröger,[4] Botden[5] and Butler[6] have recently published details of alkaline earth orthophosphates activated with tin: these also give a similar range of colours.

Preparation

The starting materials for these phosphors should be of the high purity usually associated with luminescent materials. Although a number of alternative methods are available, these phosphors have in general been prepared by combining at high temperatures the secondary strontium or barium phosphate either with the corresponding carbonate or with diammonium hydrogen phosphate. A range of compositions on either side of the pyrophosphate formula has thus been studied.

The activators tin or tin and manganese may be coprecipitated with the secondary phosphate, or may be added separately. The amount of tin needed to give the best results is not critical, the optimum amount being about 1% by weight of the matrix. Manganese, when it is effective, produces a shift in colour depending on the amount added. This is due to the gradual suppression of the emission band due to tin as the manganese band builds up.

As part of the firing process must be carried out in reducing conditions to produce the best results, it seems reasonably certain that tin is present in the stannous state. However, over-reduction may occur at this stage, leading to at least partial formation of metallic tin. This gives rise to grey body colour and marked reduction in fluorescent brightness. To compensate for this, samples may be reheated in oxidizing conditions to eliminate the body colour and increase the brightness of the product.

The temperature for these two heat treatments must be carefully chosen to obtain the best results. It is interesting to note that Butler[6] also comments on the same difficulty. He uses a mixture of nitrogen with a small proportion of hydrogen to prevent over-reduction of the tin activator in orthophosphates. No advantage has been found with this technique applied to phosphors of the type described in this paper.

Luminescent properties

Effect of tin. A range of compositions (SrO or $BaO : P_2O_5$) has been investigated with different temperatures of firing. Minor differences in colour were noted in strontium phosphates activated with tin, whereas a number of distinctive colours were obtained with corresponding barium phosphates. A summary of these results is given in Table 1, and the

spectral energy curves for these phosphors are given in Fig. 1. In the next section identification of the phases responsible for these changes is described.

The diagonal displacement in Table 1 of some of the colours is due to a change in composition at the higher temperatures by reduction and volatilization of part of the phosphorus present. Thus samples containing excess phosphate fired at the higher temperatures tend to revert to the pyrophosphate composition.

When excited by 2537 Å radiation, the intensity of fluorescence of most samples is strong: they are also excited by cathode-rays and X-rays. An interesting feature of these phosphors is the almost complete absence of thermal glow when the samples are excited at liquid-air temperatures by 2537 Å radiation and then allowed to warm up to ambient temperatures.

Effect of tin and manganese. Manganese functions as a secondary activator in strontium phosphate phosphors activated with tin. As the amount of manganese is increased the colour shifts from blue to pink through a series of whitish shades. The curves shown in Fig. 2 show the emission bands corresponding to tin and manganese. With barium phosphate phosphors, however, manganese is ineffective due probably to the inability of the much smaller manganese ion to replace corresponding barium ions. This effect is also in line with Butler's results with alkaline earth orthophosphates.(6)

Table 1. *Fluorescence of tin-activated barium phosphate phosphors*

Firing temperature (° C)	*Proportion of $(NH_4)_2HPO_4$, added to secondary barium phosphate as % (by wt.) of the barium pyrophosphate equivalent to the amount of secondary phosphate used*				
	No addition	5%	10%	15%	20%
700	green	blue-green	blue-white	yellow-white	cream
800	red	mauve	blue	blue-white	cream
900	red	pink	mauve	mauve	blue
1000	—	red	red	red	pink

Spectral energy curves of the basic phosphors responsible for the above colours are given in Fig. 1.

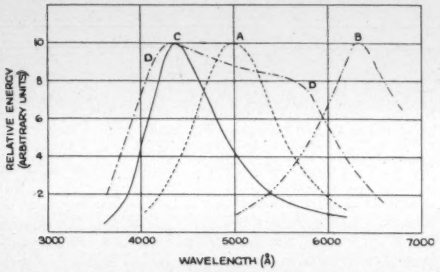


Fig. 1. Spectral energy curves of tin-activated barium phosphate phosphors

A, green; *B*, red; *C*, blue; *D*, cream.

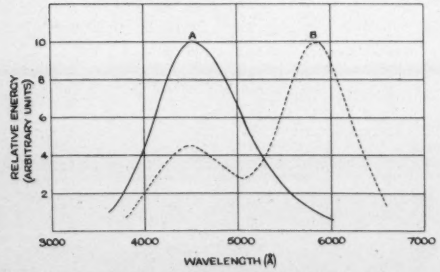


Fig. 2. Spectral energy curves of tin- and tin-manganese-activated strontium pyrophosphate

A, strontium pyrophosphate—Sn;
B, strontium pyrophosphate—Sn, 1% Mn.

X-ray investigation

Barium phosphates. Preparations corresponding to the compositions indicated in Table 1 have been examined by the X-ray powder method. The investigation showed that one of four principal phases, or mixtures of two or more of these four, account for all the colours obtained. These four phosphors will be denoted for the present by the colour of fluorescence, namely "green," "red," "cream" and "blue."

The preparations containing no excess diammonium hydrogen phosphate, and corresponding therefore to pyrophosphate composition, are responsible for the "green" and "red" phosphors and are found to be low and high temperature forms of barium pyrophosphate. No X-ray data for this compound have been previously published. X-ray spacings of the principal reflexions are given in Table 2.

With the addition to the secondary barium phosphate, of 20% diammonium hydrogen phosphate (by weight of the barium pyrophosphate equivalent to the amount of secondary phosphate used), the X-ray photographs show that one of two new phases of different structure is formed according to the temperature of firing. These are responsible for the "cream" and "blue" colours of fluorescence (the low and high temperature forms respectively).

Carefully controlled experiments involving the X-ray examination of a series of powders with compositions ranging from $2BaO.1P_2O_5$ (pyrophosphate) to $1BaO.1P_2O_5$ (metaphosphate) show that the "cream" and "blue" phases are polymorphic forms of barium tetraphosphate, $3BaO.2P_2O_5$, and this is in accord with the use of 20% excess diammonium hydrogen phosphate (Table 1). X-ray diffraction data are listed in Table 2. As with the pyrophosphate, X-ray data for this compound do not appear to have been previously recorded.

At overall compositions between the pyrophosphate and the tetraphosphate (Table 1), intermediate colours of fluorescence are obtained and the X-ray analysis shows that these preparations are in fact mixtures of two or more of the basic phosphors described above.

Strontium phosphates. Strontium pyrophosphate and tetraphosphate are responsible for the phosphors described in the earlier part of this section. The X-ray examination shows that these are closely similar in crystal structure to the low temperature forms of the corresponding barium phosphates. In the preparations examined so far, high temperature forms

Table 2. *X-ray powder diffraction data for the principal reflexions of barium and strontium phosphate phosphors. (19 cm diameter camera: CuKα radiation)*

Barium phosphates (2% Sn)								*Strontium phosphates (2% Sn)*			
$Ba_2P_2O_7$ (low temp. green fluor.)		$Ba_2P_2O_7$ (high temp. red fluor.)		$3BaO \cdot 2P_2O_5$ (low temp. cream fluor.)		$3BaO \cdot 2P_2O_5$ (high temp. blue fluor.)		$Sr_2P_2O_7$ (blue fluor.)		$3SrO \cdot 2P_2O_5$ (blue fluor.)	
d(Å)	*Intensity*	*d*(Å)	*Intensity*	*d*(Å)	*Intensity*	*d*(Å)	*Intensity*	*d*(Å)	*Intensity*	*d*(Å)	*Intensity*
7·74	s–m	3·917	vs	4·73	w–m	3·926	m–s	7·41	m–s	4·58	w
3·565	vs	3·543	m	3·808	m	3·819	s	3·448	vs	3·510	m
3·271	m	2·833	s	3·628	m	3·451	m	3·408	vs	3·394	m
3·022	m–w	2·721	m	3·505	m	3·381	m	3·132	m–w	3·199	s
2·810	s–m	2·328	m	3·326	s	3·322	s	2·904	m–w	3·026	m–w
2·654	m–w	2·266	w–m	3·127	m–w	3·202	m	2·707	m	2·950	m–w
2·323	w	2·237	m–w	3·084	m–w	3·128	m–w	2·198	m–s	2·740	m
2·301	m–w	2·159	m	2·825	m	2·820	m	2·044	s	2·669	m
2·130	s	2·113	m	2·757	m–w	2·239	m	1·867	w	2·466	w
1·940	m–s	1·962	w–m	2·550	w–m	2·192	m–w	1·849	m–w	2·104	w–m
1·727	m	1·811	m–w	2·196	m	2·150	m	1·668	w	2·019	w–m
—	—	1·772	w	2·090	w–m	—	—	—	—	—	—

vs = very strong, s = strong, m = medium, w = weak.

NOTES (1) The errors of spacings greater than 6 Å are ±0·02 Å, between 4·5 Å and 6 Å are ±0·01 Å, and below 4·5 Å are ±0·005 Å.
(2) The interplanar spacings have not been corrected for absorption.
(3) There is no correlation between the different sets of intensities.

have not been found to occur, and, with the tetraphosphate, higher temperatures of firing result in loss of P_2O_5 causing the composition and crystal structure to revert to those of the pyrophosphate. This loss of P_2O_5 also occurs in the barium phosphate system, but the temperatures involved are above those required to form the high temperature modifications.

Spacings of the principal reflexions of these two strontium phosphates are given in Table 2.

3. THE PREPARATION AND FLUORESCENT PROPERTIES OF SOME NEW COMPLEX SILICATE PHOSPHORS CONTAINING LITHIUM

The phosphors described in this section consist of complex silicates of Group Z elements (Zn, Cd, Sr, and Ba) combined with lithium and activated by manganese alone or by cerium and manganese.

Although complex silicates containing lithium are described in the literature, such compounds do not appear to have been extensively investigated for fluorescent properties. Kröger[7] mentions the fluorescence of lithium and calcium lithium silicates activated with titanium, and the fluorescence of aluminosilicates containing lithium activated with copper has also been described.[8]

Method of preparation

Starting materials for the preparation of these phosphors include the oxides or carbonates of the basic components and silica. The purity of the components should be of the high order associated with phosphor preparation. The components are mixed thoroughly either by ball-milling or hammer-milling and fired in silica vessels in a suitable atmosphere. The products are refired, if necessary, until the maximum brightness is achieved.

Luminescent properties

The most important members of this group together with their luminescent properties are described in the following sections. Whilst zinc and cadmium lithium silicates are activated by manganese alone, barium and strontium lithium silicates are activated by cerium alone or by manganese in combination with cerium.

Zinc lithium silicates. This group of phosphors[9] resembles in some respects the familiar zinc beryllium silicate family. The colour of the fluorescence may be varied from yellow-green to orange by altering the composition of the matrix or by varying the proportion of manganese activator. An atmosphere of water vapour during the firing treatment appears to assist the formation of these phosphors. The firing temperature should be about 1000° C.

The lithium content of these phosphors is not critical, but if too little is added the resulting material shows a greenish fluorescence due to the formation of zinc orthosilicate. Excess of lithium, on the other hand, reduces the luminosity and promotes the formation of "glassy" phases. The effect of the silica content is also not critical and amounts ranging from the orthosilicate to the mesodisilicate compositions have given good results. As either the silica or the manganese content is increased, the colour of the luminescence tends to shift towards the red end of the spectrum. The spectral energy curve for a phosphor containing $2ZnO.1Li_2O.6SiO_2$ (2% Mn) is shown in Fig. 3. These phosphors are strongly excited by 2537 Å radiation and are responsive

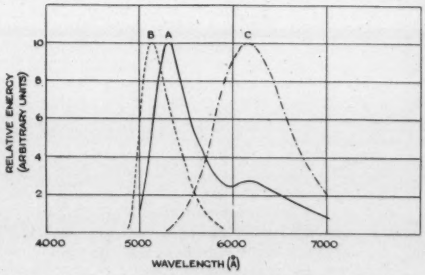


Fig. 3. Spectral energy curves of silicate phosphors containing lithium

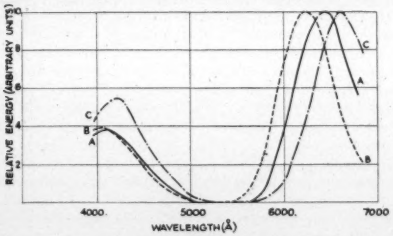
A, zinc lithium silicate, $2ZnO \cdot 1Li_2O \cdot 6SiO_2$(2% Mn);
B, cadmium lithium silicate, $1CdO \cdot 1Li_2O \cdot 1SiO_2$(1% Mn);
C, cadmium lithium silicate, $1CdO \cdot 1Li_2O \cdot 2SiO_2$(0·1% Mn).

to cathode-rays, the colour of luminescence produced varying to some extent with the different excitations.

Cadmium lithium silicates. This system[10] appears to be less complex than the zinc lithium silicates previously described. Two distinct phosphors have been prepared giving green and orange-red emission corresponding respectively to ortho- and metasilicate compositions.* These materials are fired in oxidizing conditions at about 900° C. Water vapour has no beneficial effects during firing. Equimolecular proportions of cadmium oxide to lithium oxide have given the optimum brightness with both compounds. Variation in the manganese content appears to have little effect on the colour of the orthosilicate phosphor, but with the metasilicate composition a slight shift from orange to orange-red occurs as the amount of manganese is increased from 0·1 to 1·0% by weight of the matrix.

These phosphors are strongly excited by 2537 Å radiation and by cathode-rays. Spectral energy curves for the green and orange phosphors are given in Fig. 3.

Barium strontium lithium silicates. The third group of silicate phosphors[11] is likely to prove of considerable practical importance. The group comprises a further example of a double activator system. The primary activator, cerium, gives a characteristic blue emission by itself, and acts as a sensitizer for the secondary activator manganese. As the manganese content is increased, the blue emission is reduced in intensity and the band due to manganese develops in the orange or red region. With a barium lithium silicate composition, the colour of the manganese emission is orange, and the colour becomes redder as strontium replaces barium; this effect is illustrated in Fig. 4. At higher temperatures the



(Reproduced from *Lux*)

Fig. 4. Effect of barium to strontium ratio on the emission characteristics of barium strontium lithium silicate phosphors

A, Ba/Sr ratio 1 : 1; *B*, Ba/Sr ratio 4 : 1; *C*, Ba/Sr ratio 1 : 9.

colour of the fluorescence shifts towards the yellow with those phosphors which contain manganese.

The preparation of these phosphors demands reducing conditions during firing in order to maintain cerium in the trivalent state.

The lithium content of the phosphors can be varied over a fairly wide range without producing detrimental effects and good results can be obtained with a lithium oxide molar ratio of about one fifth of the alkaline earth oxide content. Below this figure, however, the brightness of fluorescence diminishes rapidly. Although the lithium is a constituent of the complex silicate lattice it may also function as a charge compensator for the cerium activator in the manner suggested by Runciman.[12] A variation in silica content of these phosphors from approximately 2 RO : 1 SiO_2 to 3 RO : 2 SiO_2 (where R represents the combined basic radicals) gives the best results.

The excitation spectra of the phosphors shown in Fig. 5 are of a character different from those previously described. The main excitation occurs in the long wavelength ultraviolet region at about 3600 Å, whilst at shorter wavelengths

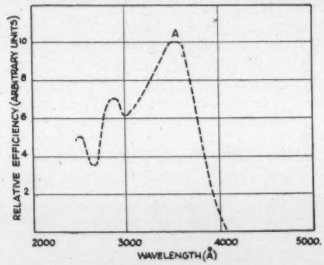


Fig. 5. Excitation spectrum of barium strontium lithium silicate phosphors

two smaller maxima occur at about 2500 and 2900 Å. This broad excitation spectrum coupled with their strong emission in the red and blue regions renders these phosphors particularly suitable for the colour correction of high pressure mercury vapour lamps.

X-ray investigation

Zinc lithium silicates. X-ray examination of preparations in this system shows that a phase of one basic crystal structure is responsible for the luminescent properties. The composition of this phase appears to be $4ZnO \cdot 2Li_2O \cdot 3SiO_2$. X-ray diffraction data are given in Table 3 for the phosphor activated with 2% Mn.

It has been found that firing in water vapour is not necessary for the formation of the above phase, though it appears to facilitate the entry of the activator.

Cadmium lithium silicates. The green and orange-red colours of fluorescence obtained in the cadmium lithium silicate system and described above have been shown by X-ray studies to correspond to the compounds $CdO \cdot Li_2O \cdot SiO_2$ (orthosilicate) and $CdO \cdot Li_2O \cdot 2SiO_2$ (metasilicate). Interplanar spacings of the principal reflexions of these phosphors are listed in Table 3.

Barium strontium lithium silicates. In the barium strontium lithium silicate system, and with the particular composition $2(Ba,Sr)O \cdot Li_2O \cdot 2SiO_2 \cdot Ce,Mn$, a continuous change of colour of fluorescence has been obtained as described above by varying the barium/strontium ratio. X-ray examination shows that a solid solution series is formed, and the change in colour from orange to red follows the replacement of barium by strontium in the crystal structure. X-ray diffraction data for the particular composition, $1BaO \cdot 1SrO \cdot 1Li_2O \cdot 2SiO_2$ are listed in Table 3.

When the lithium content is varied to cover the range $1{\cdot}2BaO \cdot 1{\cdot}2SrO \cdot 0{\cdot}6Li_2O \cdot 2SiO_2$ to $0{\cdot}75BaO \cdot 0{\cdot}75SrO \cdot 1{\cdot}5Li_2O \cdot 2SiO_2$, the colour of fluorescence remains substantially constant: X-ray examination shows that the

* Dobischek has previously given some information on cadmium silicate phosphors containing lithium (D.R.P. 747 697) but does not appear to have recognized that the introduction of lithium produces distinctive crystal phases.

Table 3. *X-ray powder diffraction data for the principal reflexions of zinc lithium silicate, cadmium lithium silicate and barium strontium lithium silicate phosphors*

(19 *cm diameter camera: CuKα radiation*)

Zinc lithium silicate $4ZnO.2Li_2O.3SiO_2$ (2% *Mn*)		*Cadmium lithium silicates* $1CdO.1Li_2O.1SiO_2$ (1% *Mn*)		$1CdO.1Li_2O.2SiO_2$ (0·1% *Mn*)		*Barium strontium lithium silicate* $1BaO.1SrO.1Li_2O.2SiO_2$ (10% Ce, 1% *Mn*)	
d(Å)	*Intensity*	*d*(Å)	*Intensity*	*d*(Å)	*Intensity*	*d*(Å)	*Intensity*
6·37	w	5·37	m–s	7·42	m	4·72	w
5·50	m–w	4·133	m–s	4·95	m	4·047	w–m
5·27	w	4·012	m–s	4·71	m–w	3·671	m
4·080	m–s	3·700	s	3·703	m–w	3·427	w–m
3·992	m–s	3·236	s–m	3·448	m–w	3·319	w–m
3·713	m–s	2·930	m–w	3·309	m–w	3·000	w–m
3·644	m–s	2·772	m	2·879	s	2·905	s
3·082	m	2·683	m	2·723	m	2·819	vs
2·748	m	2·554	m	2·578	w–m	2·391	m
2·631	s–m	2·481	m	2·336	w	2·313	m
2·518	s	2·436	m	2·300	w–m	2·021	m
1·540	s–m	2·172	m	1·769	m–w	1·932	w–m

vs = very strong, s = strong, m = medium, w = weak.

NOTES (1) The errors of spacings greater than 6 Å are ± 0·02 Å, between 4·5 Å and 6 Å are ±0·01 Å, and below 4·5 Å are ±0·005 Å.
(2) The interplanar spacings have not been corrected for absorption.
(3) There is no correlation between the different sets of intensities.

crystal structure is basically unchanged. At higher lithium contents, e.g. $0{\cdot}25BaO.0{\cdot}25SrO.2{\cdot}5Li_2O.2SiO_2$, a phase of different crystal structure can be formed, and the spectral emission becomes modified.

This is a complex system. Variations in silica content, for example, result in the formation of additional phases and changes in fluorescent properties.

4. PRACTICAL APPLICATIONS OF THE NEW PHOSPHORS

The commercial utilization of new phosphors is governed by their ability to supplement or replace existing phosphors. This will depend on factors such as special excitation and emission characteristics, luminous performance and more general considerations such as cost and ease of manufacture. Of the phosphors described in this paper the group of barium strontium lithium silicates are of immediate practical value because of their special excitation and emission characteristics. Several of the other phosphors are of potential value, but further development work is needed to assess their merits.

Tin-activated phosphors

From the practical aspect the most interesting phosphors in this group are those which show fluorescence towards the blue or red regions of the spectrum. These include blue strontium pyrophosphate, green barium pyrophosphate, red barium pyrophosphate and blue barium tetraphosphate. Blue strontium pyrophosphate which gives an efficiency at 100 hours of 25 lm/W in 4 ft, 40 W lamps may replace calcium tungstate for certain applications. The spectral emission characteristics of green barium pyrophosphate are likewise of interest to improve the colour rendering properties of the warmer types of fluorescent lighting for social purposes.

Barium strontium lithium silicate phosphors

These phosphors will probably find their main application for the colour correction of high pressure mercury vapour lamps. For this purpose a phosphor with a number of special properties is required. The excitation spectrum should extend from 2000–3800 Å while the emission band should fall predominantly in the orange to red region; some emission in the blue and blue-green region may also be an advantage. In addition, the emission should be maintained at temperatures of 150° C or higher.

In view of these stringent conditions it is perhaps remarkable that three distinct phosphor groups have recently been discovered which fulfil most of them reasonably well. They are magnesium fluogermanate,[13] magnesium arsenate,[14] and the barium strontium lithium silicates described above. A comparison of the qualities of these phosphors has been given recently[15] and a brief summary of the results is given below.

High red region ratios (i.e. percentage of total lumens passing a Wratten No. 25 filter), up to about 10% in 125 W lamps, are possible with magnesium arsenate and magnesium fluogermanate, but owing to their yellow body colour which enhances the green colour of the light, a lower red correction than is possible has to be accepted. The barium strontium lithium silicates which are almost colourless give red ratios of about 7–8% with a somewhat better blue emission than arsenate or fluogermanate. Lamps coated with the latter phosphors give chromaticity values which lie close to the black body locus.

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DISCUSSION

Dr. G. R. Fonda: There are now on record three substituted zinc silicates activated by manganese. Their spectral emissions exhibit the same position for the primary band at 5250 Å but different positions for the secondary band, 6100 Å for beryllium, 6400 Å for lithium, as reported above, and 6750 Å for barium.* This suggests that the secondary band is due to centres formed by a manganese ion associated with an ion of the particular metal substituted for zinc. Variations in the band position may well be due to the greater polarizing power of lithium and barium than that of beryllium, leading to greater distortion of the manganese orbitals.

Dr. K. H. Butler: It is interesting to note from Papers 3 and 4 that tin gives emission bands at various locations in the spectrum from long ultra-violet to the deep red regions, while the bands of manganese in silicate phosphors are by comparison almost invariant. Thus the debate on the reasons for the shift from the green emission of zinc orthosilicate to the red emission of other materials seems rather fruitless. It would be more profitable to study the tin-activated systems in detail to determine the effects of crystal structure and co-ordination number.

Dr. H. A. Klasens: In comparing the relative qualities of phosphors used for colour correction of high-pressure mercury lamps, the authors emphasize the importance of the blue emission due to cerium in the barium–strontium–lithium silicate. For practical use, however, a good temperature dependence of the phosphors is just as important, since the lamp manufacturer can thus keep to small dimensions for the outer glass bulb. In this respect the germanate is the best phosphor of the three available, with the advantage over the arsenate that it is less easily reduced under lamp operating conditions. To use the arsenate the usual N_2 filling must be replaced by CO_2. It has now been found that incorporation of 0·3 mole Li_2O per mole As_2O_5 considerably improves the temperature dependence, so that it is as good as that of the fluorogermanate, while the stability becomes quite satisfactory in N_2-filled bulbs. The effect can be explained as a special kind of induced valency. By replacing part of Mg^{2+} by Li^+ the Fermi level in the phosphor is lowered, thereby stabilizing the tetravalency of manganese. Substitution of part of the O^{2-} by F^- raises the Fermi level, and this is found to reduce the stability of the arsenate.

* Anderson, J. T., and Wells, R. S. *J. Electrochem. Soc.*, **95**, p. 299 (1949).

Mr. H. G. Jenkins: In our experience magnesium arsenate deteriorates rather rapidly at temperatures of the order of 300° C which occur in certain discharge lamps, and it will be of great interest if treatment with lithia improves the performance. Does the addition of lithia to the matrix modify the absorption band in the blue region of the spectrum?

Dr. H. A. Klasens: The absorption of magnesium arsenate in the long ultra-violet region is caused by the manganese and is not modified by the presence of lithium.

Dr. G. Günther: The poisonous properties of beryllium compounds have received much attention in the past. Has the poisonous nature of magnesium arsenate been considered, here or elsewhere?

Mr. G. Sergeant: The authors state that the discoloration of the (Sr, Ba)P_2O_7.Sn, Mn phosphor is due to reduction of the stannous compound, and that this body colour can be eliminated by heating in an oxidizing atmosphere. They also refer to the barium–strontium–lithium silicate phosphor activated by cerium and manganese, but make no specific mention of the variable grey or buff discoloration often associated with it. Can the authors explain the discoloration of this phosphor, for example as due to over reduction? Can the body colour be induced by heating in air? Have they examined the possibility of firing this phosphor in steam?

Authors' reply: In reply to Dr. Butler, 40 W fluorescent lamps coated with "green" barium pyrophosphate phosphors activated with tin have given an efficiency of about 35 lm/W after 100 hours' burning. The maintenance throughout life of the red output of colour-corrected high-pressure lamps coated with barium–strontium–lithium silicate phosphors activated with cerium and manganese has been very satisfactory.

Dr. Günther's point on the toxicity of magnesium arsenate is, of course, of considerable importance. Unlike beryllium compounds, however, the nature and effects of arsenic compounds are well known and suitable precautions in handling could be taken as in the fields of agriculture and glass technology.

The grey or buff body colour sometimes observed with barium–strontium–lithium silicates, and referred to by Mr. Sergeant, seems to be associated with the valency states of the cerium and manganese activators. If the correct balance is achieved by suitable composition and firing conditions the body colour of the resulting phosphor is almost colourless.

Paper 5

Some unusual phosphors

By S. ROTHSCHILD, Ph.D., Mullard Research Laboratories, Redhill, Surrey

An account is given of the preparation and properties of some phosphors excited by ultra-violet radiation of short wavelength, namely boron phosphate activated by thallium, and some arsenate analogues of the halophosphates; also of "self-activated" vanadates excited by ultra-violet radiation of long wavelength.

BORON PHOSPHATE

Hüniger and Panke[1] prepared phosphors by firing boric acid or phosphoric acid with suitable activators. The product consisted of low melting hygroscopic glasses. Materials of a completely different character are obtained if boric acid and phosphoric acid are brought to reaction to form boron phosphate, which is a crystalline substance insoluble in water and chemically very stable. It can be heated to a high temperature without decomposition, but at approximately 1450° C it begins to evaporate.[2] For the present investigations boron phosphate was prepared by heating a mixture of the required proportions of ammonium phosphate and boric acid slowly up to 800° C, and then at 800° C until the reaction ceased. Analysis of the product gave $66{\cdot}3 \pm 0{\cdot}3\%$ P_2O_5 and $33{\cdot}1 \pm 0{\cdot}2\%$ B_2O_3. Theoretical values are $67{\cdot}1\%$ P_2O_5, $32{\cdot}9\%$ B_2O_3 for BPO_4. The X-ray structure agreed with that found by Schultze.[3]

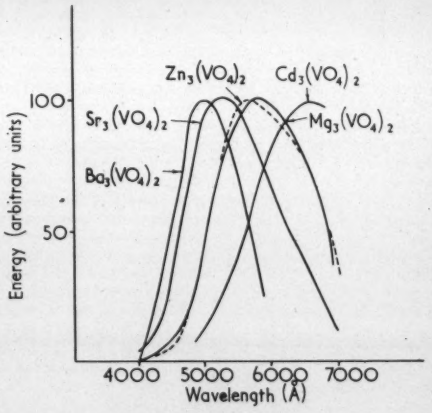
For the preparation of phosphors 5 pt of the boron phosphate were mixed with 1 pt of thallium nitrate and the mixture fired in a closed silica crucible in air for 30 min at 800° C.[4] When excited with short-wave ultra-violet radiation the resulting product had an emission peak at 3185 Å, the emission falling to zero near 3500 Å.

VANADATES

The luminescence of vanadates was first observed by Robl.[5] He found that strontium pyrovanadate, when excited by long-wave ultra-violet radiation, gave an emission between 6000–4830 Å, and barium pyrovanadate between 6000–4570 Å. The luminescence of the calcium compound was too weak to be measured. No details on preparative conditions or other characteristics were given. Weyl[6] prepared zinc vanadate phosphors by firing mixtures of 3 pt of zinc oxide with 2 pt of vanadium pentoxide at temperatures between 600 and 900° C. The colour of the fluorescence was yellow under long-wave ultra-violet excitation.

For the present investigations phosphors were prepared by mixing solutions of ammonium vanadate with nitrates of various metals. The mixtures were evaporated. the volatile matter driven off and the resulting product fired in air for 30 min at 800° C. Phosphors were made of strontium, barium, magnesium, zinc and cadmium vanadates. In all cases the highest efficiency was obtained with phosphors of a composition corresponding to $3MO \cdot V_2O_5$. Phosphors prepared from $2MO \cdot V_2O_5$ or $MO \cdot V_2O_5$ were discoloured and showed little or no luminescence. Reducing conditions also have to be avoided, otherwise compounds such as the black $ZnO \cdot V_2O_3$ may be formed. Vanadates, like tungstates, show luminescence without the addition of an activator, but only after they have been heated to a certain temperature. The addition of activators such as Tl, Pb or Sm produces no noticeable effect on the emission spectrum, and no afterglow can be observed visually after the excitation of vanadate phosphors.

These phosphors appear to be of interest as they belong to the comparatively small class of "self-activated" phosphors which includes the tungstates, molybdates and uranyl salts. Garlick[7] has pointed out that the phosphors of the tungstate type resemble impurity-activated phosphors rather than those showing luminescence without the presence of impurities, such as uranyl nitrate. Thus the afterglow of the latter material is always very short while tungstates may have a long afterglow depending on preparative conditions.[8] The emission of tungstate phosphors originates according to Randall[9] in the tungstate ion and this has been confirmed by Hameka and Vlam.[10] Henderson[11] has shown that the emission spectra of tungstate phosphors, with the exception of calcium tungstate, are very similar. The emission spectra of vanadate phosphors depend far more on the cation as shown in the figure.



Emission spectra of vanadates

ARSENATOAPATITES

Phosphors based on halophosphates of the general formula $3X_3(PO_4)_2 \cdot XY_2$ have been widely investigated. The question arose whether it might be possible to substitute arsenic for phosphorus in these compounds. It was found that the arsenatoapatite phosphors gave emissions similar to the halophosphates but of a considerably lower efficiency. A chloroarsenatoapatite phosphor was prepared by firing a mixture of 10 pt of calcium arsenate with 1·3 pt of calcium chloride, 0·25 pt of lead chloride, and 0·1 pt of manganese carbonate for 30 min at 700° C. The product was ground

and refired for 30 min at 900° C. The emission of this phosphor under excitation with short-wave ultra-violet radiation consisted of a single band nearly symmetrical on a frequency plot, with its peak at 17 100 cm^{-1} (5850 Å) and a band half-width at half peak intensity of 1200 cm^{-1}. This is very similar to the manganese band in zinc sulphide. A fluoroarsenatoapatite phosphor was prepared from 10 pt of calcium arsenate, 0·4 pt of arsenic pentoxide, 0·7 pt of calcium fluoride, 0·25 pt of manganese arsenate, and 0·35 pt antimony pentoxide.[12] This phosphor also showed a yellow luminescence, and it had the typical apatite structure. The results of a crystallographic analysis of fluoroarsenatoapatite in comparison with ordinary fluoroapatite and fermorite (a mineral in which only part of the phosphorus is replaced by arsenic), are given in the table below.

fluoroapatite Å	*fermorite* Å	*fluoroarsenatoapatite* Å
$a = 9{\cdot}36$	9·60	9·667
$c/a = 0{\cdot}735$	0·729	0·731
$c = 6{\cdot}88$	7·00	7·067

ACKNOWLEDGEMENT

I wish to thank Mr. M. G. Harwood for the crystallographic investigation of the phosphors.

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DISCUSSION

Dr. G. R. Fonda: In preparing the fluoroarsenatoapatite I have found the manganese band to be at 6100 Å rather than at 5680 Å as for the phosphoapatite. This suggests a relation between the band position and the polarizing power exerted on the manganese ion by its surroundings. The heat of formation of As_2O_5 is 40% lower than that of P_2O_5. The oxygen ions surrounding the arsenic ion thus possess a greater residual polarizing power than those round a phosphorus ion. This leads to greater distortion of the adjoining manganese ion thus causing a shift in emission to longer wavelengths.

Dr. P. W. Ranby: The phosphors described by Dr. Rothschild correspond to a BPO_4 matrix. If a molecular ratio of $1B_2O_3 : 2P_2O_5$ is used in preparation, the resulting matrix can be activated by either cerium or antimony, and in each case manganese can be incorporated as a secondary activator giving phosphors which emit strongly in the visible region when excited by 2537 Å radiation. Unfortunately these phosphors show a fairly rapid drop in brightness under high intensities of excitation, and in addition they are hygroscopic. It would be interesting to know if arsenatoapatites show any evidence of self-activation, since arsenic is known as an activator of halophosphates.

Paper 6

Electroluminescence of zinc sulphide phosphors

By K. H. BUTLER, Ph.D., and J. F. WAYMOUTH, Ph.D., Sylvania Electric Products, Inc., Salem, Mass., U.S.A.

A brief historical survey is given of the effects of electric fields on phosphors, and of recent work leading to the development of a practical light source. The phosphor preparation is described, and details of dielectric requirements, lamp construction, and optical and electrical characteristics of the lamps discussed. Reference is made to work on the effects of pulsed d.c. excitation, and on the microscopical examination of electroluminescent single crystals. Current theories of the mechanism of electroluminescence are briefly discussed.

Electroluminescence can be defined as the production of light by direct excitation of a phosphor with an electric field. Although it can be obtained with a steady direct current field under certain special conditions, it is more readily produced by application of a pulse of direct current or by application of an alternating current field. With an a.c. field, light can be produced even though the phosphor is insulated from the electrodes by suspension in a dielectric. This discovery has led to the development of a practical light source. Although the present paper will deal mainly with the practical aspects of a.c. electroluminescence, such as the preparation of the phosphors and the construction and properties of lamps, it is desirable to review very briefly the history of the subject and related work which may give an insight into the mechanism of the phenomenon.

HISTORICAL

The earliest indication that an electric field could influence the light emitted by a phosphor was the work of Gudden and Pohl[1] in 1920, who showed that application of a field to a phosphorescent zinc sulphide after excitation caused the emission of light and influenced the rate of decay. Similar later work was mainly confined to the use of d.c. fields. There was little work on the effect of a.c. fields until the study by Destriau was started in 1936.[2] The results of this have been reported in a comprehensive summary with a good

bibliography.[3] Destriau believed that there was a "provocation of luminescence in certain substances by varying electric fields of high intensity." Garlick[4] suggested that electroluminescence could be explained by liberation and acceleration of trapped electrons which caused both luminescence and also liberation of further electrons, so that the process became self-sustaining. Destriau's work was questioned by Leverenz[5] who was apparently unable to measure adequately the low light intensities obtained by Destriau.

The cell studied in greatest detail by Destriau consisted of a metal plate, upon which the phosphor, mixed with oil, was spread in a thin layer. Over this a sheet of mica was placed as insulation and a layer of "glycerined sea salt" used to form another electrode. The a.c. voltage was applied between the metal plate and the salt electrode. This simple device yielded considerable experimental data, but it was recognized as unsuitable for use as a lamp. There has been a marked revival of interest in electroluminescence since the announcement of a practical lamp.[6]

ELECTROLUMINESCENCE OF MACRO-CRYSTALS

The excitation of large single crystals of silicon carbide has been studied recently by Lehovec, Accardo and Jamgochian[7] who used electrodes in contact with the crystal, and d.c. excitation. They found that some silicon carbide crystals containing small amounts of impurities were fluorescent to ultra-violet light. Many of the same crystals showed electroluminescence, using d.c. with a cat's whisker contact. With one direction of the current, green light was emitted over a small region of the crystal, while with reverse polarity another region emitted yellow light. The currents used were from 0·5 to 200 mA and the light obtained was relatively slight.

Schön[8] has discussed the theory of light emission from silicon carbide on the basis of this and older experimental work. He believes that a *p–n* junction injects holes into an *n* region or electrons into a *p* region. Light is obtained by recombination of holes and electrons at lattice defects.

Piper and Williams[9] published in 1952 a brief note describing the luminescence of single macro-crystals of zinc sulphide containing copper. Either d.c. or a.c. voltages, applied to electrodes attached to the crystal, were effective in producing light. With d.c. the region near the cathode was identified as the source of electroluminescence and an exponential increase in light with voltage was observed. With low a.c. voltages two pulses of light appeared per cycle which were out of phase with the voltage. With high a.c. voltage, light pulses in phase with the voltage appeared and the critical potential for the appearance of these depended on the particular metal employed for the negative electrode. The current through the crystals was not reported.

Very similar results were obtained by Boer and Kummel[10] in a study of the behaviour of cadmium sulphide crystals.

PREPARATION OF ELECTROLUMINESCENT ZINC SULPHIDE PHOSPHORS

Although many phosphors have been investigated for response to electric fields, few have shown efficient electroluminescence at the voltages used. Specially prepared zinc compounds have been very effective. Destriau's best phosphors were made by heating in air at 1200° C a mixture of zinc sulphide and zinc oxide with a copper salt. The resulting powders were noticeably grey probably from CuS or CuO formed in the firing. In some cases, a part of this copper was removed by washing in ammonia. Unfortunately, the important details, necessary to allow duplication of the preparation by other workers, were not described in the published papers, so that it is difficult to evaluate these phosphors objectively.

More recent papers by Homer, Rulon, and Butler,[11] by Froelich,[12] and by Zalm, Klasens, and Diemer[13] have dealt specifically with the preparation of electroluminescent zinc sulphides.

The phosphors described by Froelich and by Zalm, Klasens, and Diemer were hexagonal in crystal structure and were prepared by firing at 1200° C. An excess of copper, above that which will go into solid solution, was employed by both groups. Froelich reported an optimum copper content of $2{\cdot}5 \times 10^{-3}$ gram atoms per mole of zinc sulphide. He employed aluminium as a co-activator and fired in a mixture of water vapour and hydrogen sulphide to obtain a grey product, which was then treated with sodium cyanide to remove excess copper. The phosphor showed green electroluminescence. A more recent letter by Froelich[14] indicated that manganese could be added to his phosphors to produce yellow electroluminescent products.

The best products by Zalm, Klasens, and Diemer also depended on the use of high copper content with firing in hydrogen sulphide at 1200°C. Their initial copper contents ranged from $1{\cdot}0 \times 10^{-3}$ to $2{\cdot}0 \times 10^{-3}$ gram atoms of copper per mole of zinc sulphide. The atmosphere during firing was also controlled so as to regulate the amount of copper actually dissolved in the lattice. They reported the preparation of blue phosphors using chloride as co-activator, and green phosphors using aluminium as co-activator.

Roberts[15] has given some experimental data on electroluminescence of a zinc sulpho-selenide, but did not describe the preparation of the phosphor.

The paper by Homer, Rulon, and Butler describes in some detail the preparation of EL phosphors. This name was given to the ZnS phosphors used in electroluminescent lamps. These EL phosphors differ considerably from previously described materials since they are cubic in crystal structure and contain lead in trace amounts. A wide range of colour, varying from a deep blue to orange, could be made by modifications of the composition. The blue EL phosphors were relatively low in copper content having 3×10^{-4} up to 6×10^{-4} gram atoms of copper per mole of zinc sulphide. Moreover, the chloride content was also relatively low. The green EL phosphors, in addition to the trace of lead, contained appreciable amounts of chloride combined with copper contents ranging from 4×10^{-4} to $1{\cdot}5 \times 10^{-3}$ gram atoms per mole of zinc sulphide. The yellow EL phosphors were made by adding manganese to the basic ingredients used for the green EL phosphors. The addition of 5×10^{-3} gram atoms of manganese per mole of zinc sulphide gave a fairly brilliant yellow; lower amounts gave greenish-yellow products. Increasing the manganese content to 2×10^{-2} gram atoms shifted the colour to a deep orange, while further increases caused a slight loss in brightness without further shift of colour.

Although lead was added to the raw materials in considerable amounts, with 2×10^{-3} gram atoms per mole being optimum for the firing method described, only trace amounts were left in the phosphor after firing; analyses showed 2×10^{-6} up to 2×10^{-5} atoms per mole. These trace amounts were essential to the development of electroluminescent response and also were found to have a considerable effect on the daylight appearance, on the ultraviolet absorption spectrum and on the fluorescent emission

spectrum. The magnitude of the effects depended upon the copper content of the phosphor.

The method of firing was one of continuous passage of the well mixed raw materials in silica trays through a heated tube. A counter-flow of nitrogen provided an inert atmosphere and carried off volatile reaction products. It was also possible to form a fluorescent powder by first firing the zinc sulphide with copper and then refiring the product with a lead compound to convert it to an EL phosphor. More recent work,[16] as yet unpublished, has shown that the flowing inert atmosphere is not needed under all conditions and that good EL phosphors can be made by firing in covered crucibles.

A treatment with hot dilute acetic acid was used with the EL phosphors to remove the excess zinc oxide added at times to the raw material mixture or formed during firing. Unlike the case of Destriau's phosphors, the use of a high zinc oxide excess in the raw material mixture was not needed, and the best phosphors were obtained with little or no zinc oxide present.

CONSTRUCTION OF ELECTROLUMINESCENT LAMPS

The practical electroluminescent lamp, in its present form, consists of a sheet of conducting glass coated with a thin layer of a solid dielectric carrying the phosphor in suspension. This layer, whose thickness is about 0·1 mm, is backed by a metallic layer in contact with it. Suitable leads are attached to the conducting surface of the glass and to the metallic layer for application of an alternating voltage. The current through the lamp depends on the area and the applied voltage. At 600 V it is of the order of 0·05 mA per cm².

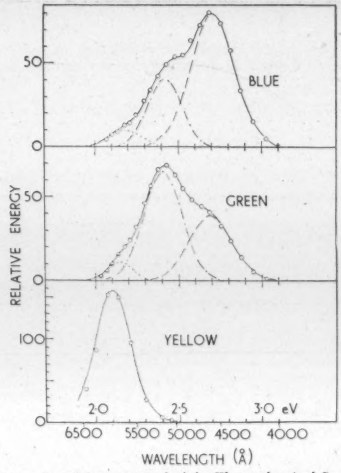
The technique of forming a conductive film on glass, by spraying it while hot with a suitable metallic salt, generally gives the most useful transparent electrode for lamp use. There are a number of alternatives for the backing conductor which are of practical value—one of the most convenient is evaporated aluminium.

The important requirements for the solid dielectric carrying the phosphor can be listed: (*a*) High dielectric constant. (*b*) High dielectric strength to alternating voltage. (*c*) High insulation resistance. (*d*) Good dispersing properties for the phosphor. (*e*) Lack of reaction with the phosphor. (*f*) Good chemical and physical stability over long periods of time. It is clear that these requirements limit the choice of materials considerably and in practice it is necessary to select a dielectric which gives the best compromise on all properties. The lamps now on the market use an alkyd resin hardened by addition of a melamine-formaldehyde or urea-formaldehyde resin. In manufacture the phosphor is dispersed in a solution of the resins, a film is formed by spraying and is converted to a solid by low temperature baking. After this, aluminium is evaporated on to the dielectric film, and protective coats applied over the aluminium. These protective coats may include a clear resin film, a wax composition, and finally a backing of glass, plastic, or metal.

ELECTRICAL AND OPTICAL CHARACTERISTICS OF LAMPS

The characteristics of the electroluminescent lamps made with cubic zinc sulphide phosphors containing lead have been described in detail by Jerome and Gungle[17] and by Waymouth.[18] Some information on the electrical behaviour of the hexagonal high copper phosphors has been presented by Diemer and Zalm[19] who used cells like Destriau's.

While the dielectric used has some bearing on the lamp characteristics, the phosphor exerts a controlling influence especially on the optical properties. Fig. 1 shows the spectral energy distribution of the light from lamps, made with typical phosphors and excited by a 60 c/s alternating voltage. The blue and green phosphors give light which can be analysed into two major Gaussian components centred at 4600 and 5200 Å and a minor component at 5800 Å. The shift in colour from blue to green results from differing amplitudes



[Reproduced from *Journal of the Electrochemical Society*]

Fig. 1. Spectral energy distribution of light emitted by electroluminescent lamps made with blue, green, and yellow EL phosphors, and operated at 60 c/s. Dotted curves show Gaussian components for the emitted light

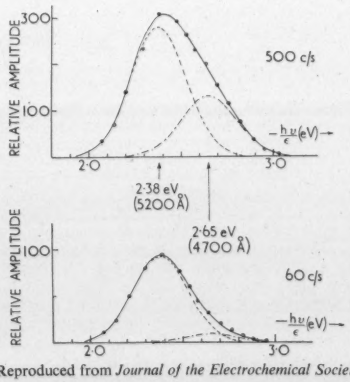


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Fig. 2. Spectral energy distribution of light emitted by a green EL phosphor in an electroluminescent lamp operated at 60 and 500 c/s.

for the two components. This difference can be attributed to the effect of composition. With increasing addition of manganese these components are gradually suppressed and a new emission band appears which is centred at 5870 Å.

Increasing the frequency of the exciting voltage applied to green or blue lamps changes the relative amplitude of the components causing a shift in colour toward shorter wavelengths. Fig. 2 shows typical results with a green lamp at 60 and 500 c/s, while Fig. 3 shows the amplitudes of the two

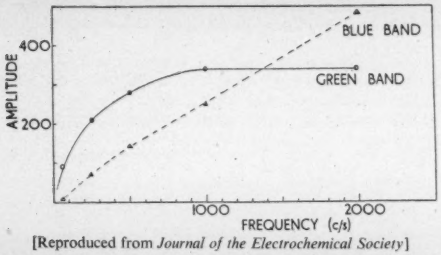

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Fig. 3. Variation of amplitude of the Gaussian components, for light emitted by a green EL phosphor, as a function of frequency of excitation at constant voltage

bands as a function of frequency. Phosphors low in manganese also show a colour shift with frequency, but those high in manganese have invariant emission. In addition to its effect on colour, changing the frequency affects the light output. This is shown in Fig. 4 for green lamps. At low frequencies the brightness increase is nearly linear with

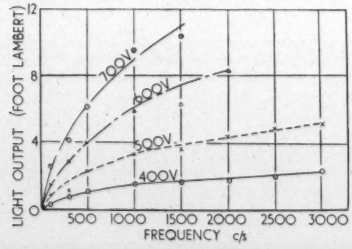

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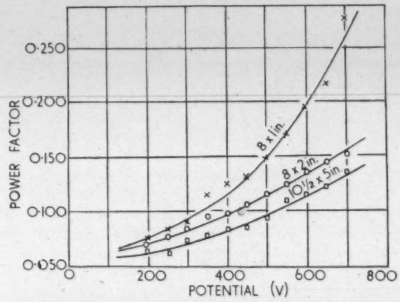
Fig. 4. Variation of surface brightness of a green electroluminescent lamp as a function of the frequency of excitation

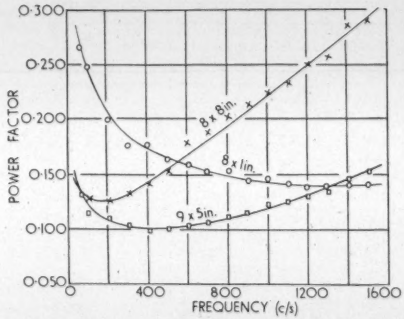
frequency, but there is a tendency to saturate at high frequency. This can be explained by the saturation of the green emission at high frequency, seen in Fig. 2. The effect of voltage on light output varies with the range considered. At low voltages the relation between brightness and voltage can be expressed approximately either by an exponential function or by a power law with an exponent close to 5. At higher voltages the relationship is nearly linear.

The electrical behaviour of the lamp can be described as that of a condenser with resistors in series and in parallel. A non-ohmic resistance is needed to describe the behaviour completely and this resistance property can be ascribed to the presence of the phosphor. Fig. 5 shows the effect of voltage on power factor and Fig. 6 the effect of frequency for several different sizes and shapes of lamps.



[Reproduced from *Journal of the Electrochemical Society*]

Fig. 5. Variation of the power factor of electroluminescent lamps made with green EL phosphors as a function of the applied voltage at 60 c/s



[Reproduced from *Journal of the Electrochemical Society*]

Fig. 6. Variation of the power factor of electroluminescent lamps as a function of frequency for various sizes of lamp

RESPONSE OF PHOSPHORS TO PULSED DIRECT CURRENT

Waymouth and Bitter[20] have found some unusual phenomena when a d.c. pulse is applied to green EL phosphor crystals suspended in a solid dielectric. If the field is applied for no more than a few hundred seconds, the initial application of the field gives no light, but subsequent removal of the field gives burst of light. After this, light is emitted both on application and on removal of the field. The light output is not affected by the rate of rise of the d.c. field, but is determined solely by the maximum field in the phosphor.

On the other hand, if the field has been applied for a time exceeding a few hundred seconds, the behaviour is reversed. No light is emitted on the first removal of the field but light is observed, both when the field is applied again and also on subsequent removal after a short interval. Thus, the light emitted is dependent on the previous charging history of the

sample. This curious result has been explained by assuming both a "charged" and a "discharged" equilibrium condition. It was also found that phosphors placed in a d.c. field develop a "frozen" electric dipole moment, and Waymouth and Bitter believe that the dependence of light output on charging history is a consequence of the frozen dipole moment developed when the phosphor is in an electric field.

MICROSCOPIC OBSERVATIONS

Additional work has been reported by Waymouth and Bitter[20] on the effect of field direction and strength on the light output of individual crystals of cubic zinc sulphide, activated by copper and lead, when observed under the microscope at a magnification of 200 diameters.

In an a.c. field the crystals show electroluminescence in two types of localized bright spots. The first type is found at the junction of two crystallites which are portions of an aggregate. The second type is found at the end of a long needle-shaped crystallite. Fig. 7 shows a plot of the lowest

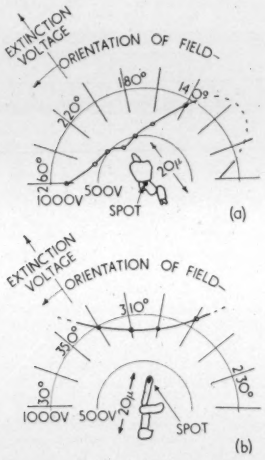


Fig. 7. Variation of the voltage, necessary to produce microscopically observable light, with direction of the electric field; (*a*) junction type spot [Reproduced from *Physics Today*]; (*b*) needle type spot

voltage at which light can be observed (the "extinction" voltage) against the orientation of the field with respect to the luminescing spot.

With the junction spot the brightness is a maximum when the field direction is at right angles to the plane of the junction. In contrast, the needle spot is brightest when the field is parallel to the long axis of the needle. Either type of spot emits light once per cycle with the peak in light output being somewhat out of phase with the applied voltage. The amount of light is nearly linear with respect to the amount of applied field above a threshold.

MECHANISM OF ELECTROLUMINESCENCE

The methods used to prepare the more efficient electroluminescent zinc sulphides suggest that the phosphor particles are not homogeneous. The dark colour indicates that in addition to the zinc sulphide crystallites containing copper in solid solution, some other phase is present. Since EL phosphors can be made by exposing a suitable phosphor to a lead-bearing atmosphere, it seems probable that this other phase exists either at the surface of the crystal or at a junction between two crystallites. This second phase may be copper oxide, copper sulphide, zinc sulphide of higher copper content, or zinc oxide—possibly of high copper or manganese content. This hypothesis is confirmed by the microscopic observation that electroluminescence occurs only at localized spots in the crystal.

This inhomogeneity of the phosphor particles makes it possible that the electric field across a particle suspended in a dielectric may, in fact, be concentrated across a barrier layer at the luminescing spot. If this be true, then electric fields above 10^6 V per cm may exist within the luminescing spots. With such fields plausible mechanisms for the direct transfer of energy from the electric field to the activator centres can be postulated on the basis of motion of electrons or holes. Two likely mechanisms have been suggested:

Excitation by collision. Electrons from donor centres are freed either thermally or by the electric field, and enter the conduction band. There they are accelerated by the field until they have kinetic energies sufficient to excite or ionize activator centres.

Direct field ionization. This mechanism requires that in a strong electric field, electrons in bound states of activator centres may escape to the conduction band by wave mechanical tunnelling—a process similar to the Zener emission.[21]

It should be noted that the mechanisms of electroluminescence, for the two distinct cases of insulated small particles suspended in a dielectric and of large single crystals in contact with electrodes, may be quite different. Application of a theory proposed for one type of electroluminescence to the other type should be considered with caution and with due regard for the major difference in boundary conditions and in magnitude of the electrical currents in the phosphor.

FUTURE DEVELOPMENTS

Electroluminescence has developed in the past few years from a laboratory curiosity, which could be seen only by the dark adapted eye, to a point where it is a practical light source of considerable usefulness. The increase in brightness and efficiency has been at least one hundred-fold, though probably less than one thousand-fold. While progress may be slower in the future, it can be expected that further improvements will be made.

The fact that electricity can be directly converted into light has already shown that changes in the theory of fluorescence will be required. At present workers in this field are feeling their way towards a suitable theory, with progress limited by lack of experimental data. The availability of improved phosphors makes accumulation of such data much easier and there should be a considerable advance in the theoretical approach in the near future. Since electroluminescence is seemingly connected with surface effects of solids with lattice defects, it is probable that development of an adequate theory may throw light on other difficult problems of surface states of solids.

ACKNOWLEDGEMENTS

Many of the developments reported in this paper are the results of the co-operative work of a group investigating electroluminescence under the direction of Dr. E. F. Lowry.

Most of them appear as co-authors of papers (see References) and we wish to express our thanks to all members of the group for their contributions to this paper.

We wish also to thank Mr. O. H. Biggs and Dr. E. F. Lowry for their intense interest and invaluable suggestions on both practical and theoretical problems of electroluminescence during the progress of the development.

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DISCUSSION

Mr. H. G. Jenkins: Could the authors give some information on the brightness, luminous efficiency and maintenance during life of the electroluminescent panels just demonstrated? We have made panels which appear to be similar in brightness but giving only 50% of their initial light output after 1000 hours' burning. On the other hand, we have obtained values as high as 90% after 3000 hours' burning from electroluminescent lamp bulbs where the ingress of moisture can be effectively prevented.

Mr. H. W. Windebank: No reference appears to the current waveform or to its phase displacement with voltage on any of the oscillograms. Figures of capacitance and conductance current per unit area and the d.c. charging and absorption charging currents, all taken on a panel for which an oscillogram is available, would help in a better appreciation of the mechanics of composite panels.

Authors' reply: On 600 V, 60 c/s operation we have made production runs to a specification of 5 foot lamberts. The luminous efficiency is difficult to determine accurately because of the low wattage but we believe it to be about 3–5 lm/W.

For lamps with organic dielectrics the loss of brightness during life is due to a decomposition of the phosphor in the presence of moisture akin to photochemical blackening, and the decomposition is accelerated by an electric field. Our quality testing required less than a 10% drop in 300 hours at 100° F and 100% relative humidity. This accelerated life test corresponds to more than 1000 hours' normal burning. Hermetic sealing of the lamp was essential with this dielectric. With the glass dielectric lamps demonstrated this afternoon, the problem of loss of brightness is much less severe, and less than a 10% drop is found after several thousand hours' operation.

In reply to Mr. Windebank, some data of this type will be found in references (17) and (20) of our paper.

Paper 7

The mechanism of electroluminescence of zinc sulphide

By W. W. Piper, Ph.D., and F. E. Williams, Ph.D., General Electric Research Laboratory, Schenectady, N.Y., U.S.A.

The impact excitation mechanism of electroluminescence is formulated and applied to the electroluminescence of ZnS . Cu crystals. A barrier similar to the Mott–Schottky exhaustion barrier exists in the crystal at each electrode. Quantum mechanical tunnelling through the barrier yields excitation in phase with the applied alternating voltage, as well as d.c. electroluminescence. Both shallow and deep donors in the exhaustion layer are prerequisite for excitation out of phase with the applied alternating voltage, and a continuous energy distribution of deep donors yields the experimental dependence on voltage of the intensity of the out of phase component of electroluminescence. Several donor distributions are theoretically analysed in detail. The conduction electrons which deviate from average behaviour by experiencing fewer collisions with lattice vibrations, thereby attaining high velocities with fields below breakdown values, probably are of importance to the mechanism. The actual excitation of the luminescence centre may be accomplished by capture of electron-hole pairs formed by impact ionization.

The direct conversion in a semiconducting solid of electrical energy into luminescence is now being investigated extensively. The excitation of luminescence by the application of an electric potential to a crystal or to a suspension of crystals is termed "electroluminescence."

The excitation by an applied potential of light emission from silicon carbide crystals was investigated by Lossev.[1] Either an alternating or direct voltage can be applied with point contact electrodes directly to a silicon carbide crystal. The light emission is localized in regions near the electrodes. Tetzner[2] demonstrated that the emission at the cathode is solid-state luminescence. Lehovec, Accardo, and Jamgochian[3] showed that the yellow emission of silicon carbide occurs at p–n junctions when a voltage is applied in the forward direction, and proposed that the electroluminescence occurs as a result of the optical recombination of charge carriers injected across the p–n junction. More recently, Haynes and Briggs[4] have reported the emission of radiation arising from injection in p–n junctions of germanium and silicon. The emission is, of course, in the infra-red region and is due to the direct recombination of an electron at the bottom of the conduction band and a hole at the top of the filled band.

Destriau[5] extensively studied the electroluminescence of sulphide phosphors in alternating fields. Roberts[6] has reported quantitative measurements and calculations on improved electroluminescent cells consisting of copper-activated zinc sulphoselenide suspended in various thermoplastic dielectrics. Piper and Williams[7] have reported both a.c. and d.c. electroluminescence in single crystals of copper-activated zinc sulphide and have proposed the impact excitation mechanism of electroluminescence. D. Curie[8] has also recognized the relevance of the theory of dielectric breakdown to electroluminescence. The present paper develops the impact excitation mechanism in detail and applies the theory quantitatively to ZnS . Cu crystals.

EXPERIMENTAL RESULTS

The characteristics of electroluminescence in zinc sulphide type phosphors have been experimentally determined with powder phosphor cells[6,9] and with large single crystal phosphors.[7] Any proposed mechanism of electroluminescence should be able to explain most if not all of these characteristics. When certain activated zinc sulphide phosphors are placed in an alternating electric field they emit light characteristic of the activator. Furthermore, the pulses of light are considerably out of phase with respect to the peak voltage, and the light appearing in alternate half cycles originates in different regions of the phosphor crystal. The excited region is always on the side of the crystal nearer that electrode which is changing in the direction of more negative voltage. If the emitted light is studied as a function of voltage at constant frequency, a threshold is observed above which the light increases superlinearly. At high voltages the curve asymptotically approaches a straight line on a log-log plot corresponding to a power of between two and three (i.e., $B \propto V^n$; $2 < n < 3$). The light also increases proportionally to the frequency at low frequencies, but above 1 kc/s some saturation effects become evident. Furthermore, the integrated light output produced by a triangular pulse of voltage depends on the peak voltage, but is independent of the width of the base between 5×10^{-5} sec and 0·5 sec. The voltage and frequency characteristics are only slightly dependent on temperature. In single crystal experiments where the metal electrodes are directly in contact with the crystal, electroluminescence is also observed upon application of a direct potential. The threshold potential for this effect is larger than that for the out of phase electroluminescence, and for a given crystal it varies with the electrode material used. The light emitted is directly proportional to the current passing through the crystal. This current increases exponentially with voltage above the threshold.

PROPOSED MECHANISM

Theoretically there are several conceivable mechanisms for the excitation of luminescent solids by an applied potential: (1) The activator system could be field-excited or field-ionized directly with sufficient applied voltage. (2) Appropriate injected minority charge carriers could be captured by the activator system which is thereby ionized. Either a p–n junction or suitable surface states are prerequisite to the carrier injection mechanism. (3) Conduction electrons having sufficient kinetic energy could, by impact, excite or ionize the activator system, or ionize the lattice, thereby producing electron-hole pairs which recombine at the activator system.

To estimate the field necessary to accomplish direct-field excitation or ionization of the activator system, comparison was made with the work of Lanczos[10] on field ionization of atomic hydrogen. Lanczos calculated that a field of 7×10^5 V/cm is necessary to ionize atomic hydrogen from the state $n = 5$ which is 0·54 eV deep and that the necessary

field varies as the square of the depth of the level. Since the ground state of the activator system in ZnS.Cu is about 3 eV below the conduction band the ionization field is 2×10^7 V/cm. An even higher field is predicted by the approximate formula of Frenkel.[11] The excitation field is essentially the same since the emitting state is only 0·2 eV below the conduction band. Direct-field excitation of the activator system seems unlikely since the required field is well in excess of the breakdown field of ZnS.

The carrier injection mechanism does not seem involved in the electroluminescence of ZnS.Cu for several reasons: (*a*) A threshold of the order of 10^2 V would not be expected. (*b*) The appropriate minority charge carriers to excite the activators in the bulk of the crystal are positive holes; therefore, in contradiction with experiment, excitation in the region of the anode would be expected. (*c*) There is no evidence of either *p–n* junctions or suitable surface-states in electroluminescent ZnS.Cu.

The impact excitation or ionization mechanism is in accord with the electroluminescent and related properties of ZnS.Cu. Electrons in donor states approximately 0·5 eV below the conduction band could be field-excited to the conduction band at reasonable field strengths, and they would then have some chance of acceleration to kinetic energies sufficient for the impact excitation or ionization of activators. These traps are also deep enough not to be emptied thermally during the voltage cycle.

The dielectric breakdown field for pure zinc sulphide is greater than 10^5 V/cm and probably less than 10^6 V/cm, the critical field for the alkali halides. The three current models for dielectric breakdown[12,13,14] agree that the probability of an electron being accelerated to high kinetic energy at fields less than 1/10 the field for breakdown is quite small. Roberts[6] has estimated the average field inside the crystal particles in electroluminescent powder cells to be less than 10^4 V/cm at the threshold of electroluminescence. Average fields can also be estimated easily in electroluminescent single crystals and at the threshold are again less than 10^4 V/cm. Immediately a barrier is suggested so that the local field in a particular part of the crystal will be increased to near the breakdown field.

At least two possible types of barrier should be considered: (1) A chemical barrier having a different composition from the bulk of the phosphor. (2) An exhaustion barrier similar to the Mott–Schottky barrier.[15] Both types would be expected, from physical considerations and from the data on electroluminescence, to be near the surface. The source of the electrons for the out of phase component of a.c. electroluminescence is difficult to attribute to a strictly chemical barrier whereas it follows naturally from the exhaustion barrier. In addition, the dependence of the barrier height and width on the work function of the electrode material is in accord with the characteristics of an exhaustion barrier. Therefore, although some difference between the composition of the barrier and the bulk of the crystal, particularly in donor concentration, cannot be excluded, the barrier will be regarded as primarily of the exhaustion type.

The ground and excited states of the copper activator centres in ZnS are between the valency band and the conduction band about 3 eV apart.[16,17] Since the band gap is only 3·7 eV the unexcited activators are hole traps. Thus ZnS.Cu is most likely an *n*-type semiconductor of high resistivity. If the work function is less than that of a metal electrode in intimate contact at the surface, donors next to the surface will ionize until a sufficiently wide space charge layer has been created to equalize the Fermi level in the phosphor and in the metal.

If the crystal lies between two similar electrodes at different potentials, electrons will move across the crystal and into the anode easily, but a potential barrier at the cathode equal in height to the difference in work functions will prevent the movement of electrons from the cathode into the crystal. The exhaustion layer next to the cathode will broaden until the entire potential difference is across the exhausted region of the crystal. As the applied potential is increased the magnitude of the field next to the cathode increases until the potential barrier arising from the difference in work functions is so thin that it can be penetrated by electrons from the cathode. A direct current will flow through the crystal above this critical voltage.

Below this threshold conduction electrons must originate within the crystal. An alternating potential applied between the electrodes will alternately deplete and replenish exhaustion layers at the electrodes. After the first few voltage cycles electron traps will behave in many respects like donors. If the donor levels lie at different depths below the conduction band, the deeper ones will be field-ionized. The necessary field to excite the electron from a deep donor will vary with the depth of the donor. The conduction electrons from sufficiently deep donors will be in a strong enough field to be successfully accelerated to large kinetic energies; that is, they will gain energy from the field more rapidly than they will lose it to the lattice by phonon emission. At energies above 3 eV these electrons will be capable of exciting by impact activator atoms (which can then be thermally- or field-ionized) and above 3·7 eV these electrons can begin to excite valency electrons to the conduction band. Some of the holes created by the excitation of valency electrons will be captured by activator centres, which become ionized. Subsequent capture of electrons from the conduction band leaves the activator systems in the emitting state.

It is not necessary that the local field be sufficient to accelerate the average electron field-ionized from a donor. Seitz[14] has shown that the probability of a conduction electron in a field E having relatively few collisions with the lattice vibrations and thereby attaining sufficient kinetic energy for impact excitation is:

$$P = e^{-C/E}$$

where C is a constant dependent on the field required for accelerating the electron that experiences the average number of collisions. All the conduction electrons absorb energy from the field but only those field-ionized from relatively deep donor levels and subsequently experiencing relatively few collisions with lattice vibrations contribute to impact excitation of the activators. The rather low efficiency of electroluminescence is therefore not surprising.

DETAILED CHARACTERISTICS OF THE BARRIER

A. Mott–Schottky exhaustion barrier. For mathematical simplicity consideration will be confined to the case of a single crystal phosphor in intimate contact with plane, parallel electrodes. The thickness of the crystal is small compared to the electrode dimensions so that edge effects may be neglected. If an electric potential difference is applied between the electrodes, an exhaustion layer will form next to the cathode as described in the previous section. Let

V_0 = the applied potential which is large compared to the difference of work functions,

N = the density of electron donors,
ϵ = the dielectric constant of the crystal,
d = the width of the exhaustion layer,
x = the distance into the crystal from the cathode.

In the exhaustion region the positive space charge density will be Ne; no space charge will exist in the bulk of the crystal. Substituting in Poisson's equation

$$dE/dx = 4\pi Ne/\epsilon \tag{1a}$$

and integrating

$$E(x) = (4\pi Ne/\epsilon)x + C \tag{2a}$$

Substituting the boundary condition $E(d) = 0$ into equation (2*a*) and defining $A = (8\pi Ne/\epsilon)^{\frac{1}{2}}$

$$E(x) = \tfrac{1}{2}A^2(x - d) \tag{3a}$$

If an electron at the cathode has a potential energy of V_0, with respect to the anode, then

$$V(x) = -\int_x^d E(x)dx = \tfrac{1}{4}A^2(d - x)^2 \tag{4a}$$

Combining equations (3*a*) and (4*a*), then

$$E(x) = -A\,[V(x)]^{\frac{1}{2}} \tag{5a}$$

$$d = \frac{2V_0^{\frac{1}{2}}}{A} \tag{6a}$$

B. Excitation of the activator centres. In the previous section the donor levels were assumed to be shallow enough to be easily ionized either thermally or by a field corresponding to a very low voltage applied between the electrodes. Electrons introduced into the conduction band in a high field portion of the exhaustion layer, if originating within the crystal, must come from donor levels well below the conduction band which are ionized for values of the local field, $E \geqslant E_c$, the critical value for ionization. If ξ is the depth of the donor in electron volts then

$$E_c = B\xi^2 \text{ V/cm} \tag{1b}$$

and $B = 2{\cdot}4 \times 10^6$ if one assumes that the deep donors are sufficiently localized so that Lanczos' calculations for hydrogen do not need correcting for the surrounding dielectric medium. The effect of the dielectric medium is to increase E_c for a given ξ. The easiest donor distribution to analyse is deep donors of a single depth and in much lower concentration than the shallow donors. The field in the barrier will then be governed by the shallow donors. Regardless of position in the barrier, each electron from a deep donor upon being emptied by the field E_c will be in the same field configuration relative to its position at the time of its release. Thus each electron released from a deep donor has the same probability of impact excitation before leaving the barrier region. Let

n = the density of deep donors,
η = average number of photons produced by each electron released from a deep donor.

Then the number of photons released per unit cross-section of the electrodes upon application of a voltage V_0 is

$$\phi = na\eta \tag{2b}$$

where, as shown in Fig. 1, a is the distance from the surface into the crystal to the plane where the field equals but does not exceed E_c. Substituting equation (6*a*) into equation (3*a*)

$$E_c \equiv |E(a)| = AV_0^{\frac{1}{2}} - \tfrac{1}{2}A^2a \tag{3b}$$

If we also define the voltage, V_c, as that applied voltage which produces a field E_c at $x = 0$, then utilizing equation (5*a*), equation (3*b*) may be solved to give

$$a = \frac{2}{A}(V_0^{\frac{1}{2}} - V_c^{\frac{1}{2}}) \tag{4b}$$

Substituting equation (4*b*) into equation (2*b*)

$$\phi = G(1 - \beta)V_0^{\frac{1}{2}} \tag{5b}$$

where $G = 2\eta n/A$

and $\beta = (V_c/V_0)^{\frac{1}{2}}$ (6*b*)

If an a.c. signal is applied between the electrodes, the maximum width of the exhaustion layer will exist at an electrode when that electrode is at the peak negative voltage. As the electrode becomes less negative the exhaustion region

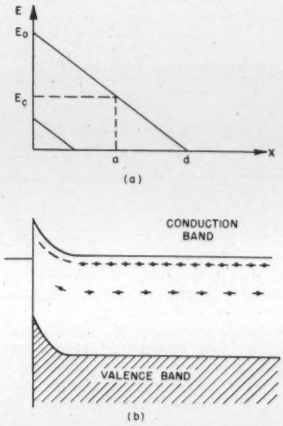

Fig. 1(*a*). Field distribution near the cathode for an exhaustion layer with uniform space charge density. (*b*) Band picture of an *n*-type semiconductor in intimate contact with a metallic electrode

will shrink and at the same time an exhaustion layer will grow at the opposite electrode until the second electrode is at its peak negative value. The changes during a voltage cycle are shown in Fig. 2.

Deep donors are being emptied only during that part of the cycle when the exhaustion layer is increasing in width, and are replenished in the other half of the cycle. If the high energy electrons only excite activator centres, all the light from a particular exhaustion region will occur while the deep donors are being emptied. However, if activators are ionized or if holes are created in the valency band, additional light will appear at a later time. Only the first case will be examined in detail.

Using the lower edge of the conduction band in the bulk of the crystal as the zero reference of potential, the electrode potential which appears at alternate electrodes on alternate half cycles when a sinusoidal e.m.f., $V_p \cos \omega t$, is applied is

$$V_0(t) = \tfrac{1}{2}V_p(1 \pm \cos \omega t); \quad \begin{matrix} - = (0 \leqslant \omega t \leqslant \pi) \\ + = (\pi \leqslant \omega t \leqslant 2\pi) \end{matrix} \tag{7b}$$

and

$$\beta^{-2} = \frac{V_p}{2V_c}(1 - \cos \omega t);\ 0 < \omega t < \pi \qquad (8b)$$

Substituting equation (8*b*) into equation (5*b*) and differentiating

$$d\phi/dt = \frac{\omega G(V_p/8)^{\frac{1}{2}}}{(1 - \cos \omega t)^{\frac{1}{2}}} \sin \omega t \qquad (9b)$$

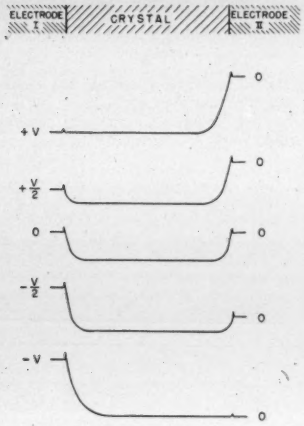

Fig. 2. Potential distribution at various times during a voltage cycle with an a.c. sinusoidal e.m.f.

Fig. 3 shows the instantaneous emission of light as a function of time, equation (9*b*), over a half cycle of voltage. At a constant peak applied voltage this idealized case would produce photons at an average rate directly proportional to the frequency, in agreement with experiment. The general

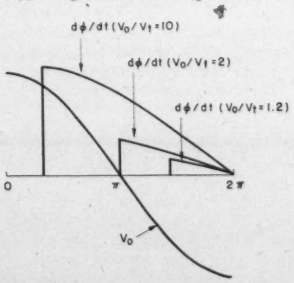

Fig. 3. Instantaneous light emission over one half a voltage cycle for the case of a single deep donor energy. Three values of peak applied voltage are portrayed

shape and change of shape and position with voltage is roughly in accord with experimental observations on single crystals of ZnS.Cu. However, at voltages well above the threshold, the calculated brightness increases as $V_0^{\frac{1}{2}}$ in contradiction to the experimentally determined square- to cube-law dependence. (See Fig. 6.)

C. Distribution of deep donors. A continuous energy distribution of donor levels seems a more realistic approximation in zinc sulphide in the light of experimental determinations of trap distributions in this phosphor. It is easiest to calculate a distribution in energy of deep donors, say below ξ_1, with the total concentration of deep donors much less than that of shallow donors; as a result the shallow donors still determine the potential distribution in the exhaustion layer.

If we let

$n(\xi)d\xi$ = density of deep donors between ξ and $\xi + d\xi$,

N = density of shallow donors,

and require $$N \gg \int_{\xi_1}^{\infty} n(\xi)d\xi,$$

equation (3*a*) again describes the electric field in the barrier.

With a distribution of donor depths the efficiency of photon production as a function of initial field intensity must be assumed. A simple function, which over-emphasizes the effect of the shallower donors, results from the assumption that the efficiency factor is proportional to the drop in potential experienced by the electron from the point where it is released to the point where it reaches the threshold field, E_t, below which it cannot be successfully accelerated. Then

$$\eta = G'[V_c(\xi) - V_t]$$
$$= \frac{G'}{A^2}[E_c^2(\xi) - E_t^2] \qquad (1c)$$

where G' is a constant. The deep donor distribution which approximates a uniform one and is readily integrated is

$$n(\xi)d\xi = n_0\xi d\xi. \qquad (2c)$$

Over the range of experimental interest ($V_0 < 10V_t$) the deepest donor emptied is only $1{\cdot}8\ \xi_1$, if ξ_1 is the depth of the donors emptied at the threshold voltage, V_t. From equation (1*b*) donors $(E_c/B)^{\frac{1}{2}}$ deep are emptied at a field E_c. Defining E_0 and using equation (5*a*):

$$E_0 \equiv |E(0)| = AV_0^{\frac{1}{2}}.$$

Utilizing this equality and solving equation (3*b*) for a, the number released within $\frac{1}{2}dE_c$ of the field E_c over one half cycle is:

$$n(\xi)ad\xi = (n_0/A^2B)(E_0 - E_c)dE_c$$

and the contribution to the integrated light from the donor is

$$d\phi = na\eta d\xi = \frac{G}{A^4}(E_0 - E_c)(E_c^2 - E_t^2)dE_c \qquad (3c)$$

where $$G = n_0G'/B.$$

Integrating over all energy levels concerned, the total photon emission for one half cycle is

$$\phi = (G/A^4)\int_{E_t}^{E_0}(E_c^2 - E_t^2)(E_0 - E_c)dE_c. \qquad (4c)$$

Integrating

$$\phi = \frac{1}{12}G(1 + 3\gamma)(1 - \gamma)^3V_0^2 \qquad (5c)$$

with $$\gamma = (V_t/V_0)^{\frac{1}{2}}.$$

Thus a continuous distribution of deep donors yields a voltage dependence of brightness in closer agreement with experiment. The instantaneous light output as a function of

time ($d\phi/dt$) was calculated as for the single level case and is shown in Fig. 4 for three values of γ.

By choosing a radically different donor distribution an evaluation of the sensitivity of the voltage dependence with

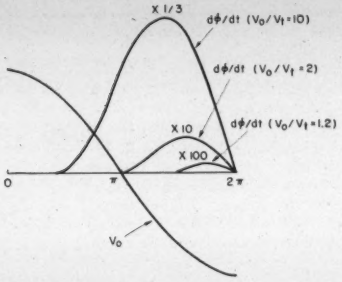

Fig. 4. Instantaneous light emission over one half a voltage cycle for the case of a linear energy distribution of deep donors. Three values of peak applied voltage are portrayed

the variation of trap distribution may be made. An exponentially decreasing distribution has been selected. In order to obtain an integral with an exact solution the distribution

$$n(\xi)d\xi = n_0\xi e^{-\alpha\xi^2/\xi_i^2}d\xi \qquad (6c)$$

has been chosen. In Fig. 5 this distribution ($\alpha = 1$, 2, and 4) is compared with the distribution used in the last example over the range of donor depths of interest. The field configuration will no longer be linear in x. However, a linearly

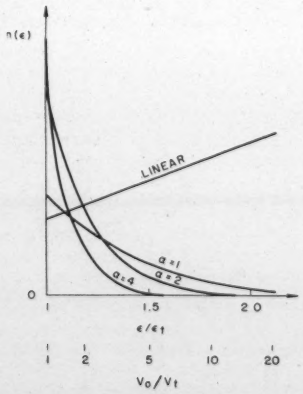

Fig. 5. Distribution of deep donors for the four cases analysed. The curves have each been multiplied by a different arbitrary constant

varying field becomes an increasingly better approximation as α increases and will be used to permit an analytical solution.

Using the same efficiency function (1*c*) and the exponential donor distribution (6*c*), the contribution to the light output integrated over one half cycle of the donors associated with fields within $\frac{1}{2}\,dE$ of E_c is

$$d\phi = \frac{G}{A^4}(E_c^2 - E_i^2)(E_0 - E_c)e^{-\alpha E_c/E_i}dE_c \qquad (7c)$$

and the total integrated light is

$$\phi = \frac{G}{A^4}\int_{E_t}^{E_0}(E_c^2 - E_i^2)(E_0 - E_c)e^{-\alpha E_c/E_i}dE_c \qquad (8c)$$

The value of this integral varies with α:

for $\alpha = 1$

$$\phi = GV_i^2\left[\frac{4 - 14\gamma}{\gamma e} + \frac{1 + 4\gamma + 5\gamma^2}{\gamma^2\exp(1/\gamma)}\right] \qquad (9c)$$

for $\alpha = 2$

$$\phi = \frac{1}{8}GV_i^2\left[\frac{6 - 13\gamma}{\gamma e^2} + \frac{2 + 4\gamma + \gamma^2}{\gamma^2\exp(2/\gamma)}\right] \qquad (10c)$$

for $\alpha = 4$

$$\phi = \frac{1}{128}GV_i^2\left[\frac{20 - 31\gamma}{\gamma e^4} + \frac{8 + 8\gamma - 5\gamma^2}{\gamma^2\exp(4/\gamma)}\right] \qquad (11c)$$

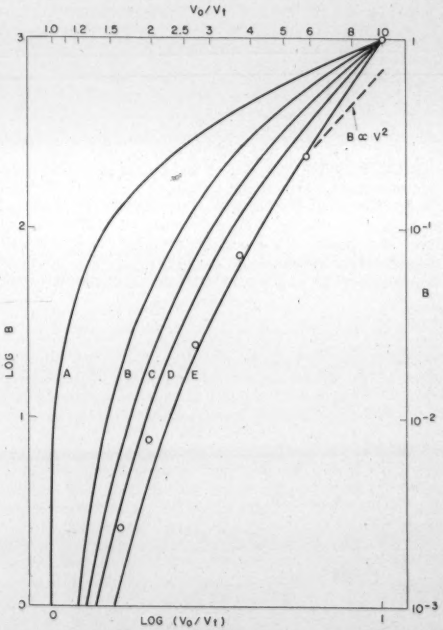

Fig. 6. Integrated light output as a function of voltage for the analytical expressions and for a typical set of experimental points for a single crystal. The curves have been adjusted by constant factors to coincide at ten times the threshold voltage

A, single deep donor level, equation (5*b*); *B*, exponential distribution of deep donor levels, $\alpha = 4$, equation (11*c*); *C*, exponential distribution, $\alpha = 2$, equation (10*c*); *D*, exponential distribution, $\alpha = 1$, equation (9*c*); *E*, linear distribution, equation (5*c*); (○) experimental points.

A plot of brightness as a function of applied voltage for equations (5*b*), (5*c*), (9*c*), (10*c*) and (11*c*) is shown in Fig. 6. The brightness is in arbitrary units and functions have been normalized to coincide at $V_0/V_1 = 10$. The experimental dependence of brightness on applied voltage results from the continuous distribution in energy of the donor levels and is clearly rather insensitive to the detailed donor distribution function.

CONCLUSIONS

The impact excitation mechanism of electroluminescence is in accord with the experimental data on ZnS.Cu, whereas the direct-field excitation of the activator and the charge carrier injection mechanism are in distinct conflict with these data. The applied voltage is localized by a cathode barrier of the exhaustion type. In phase a.c. electroluminescence and d.c. electroluminescence in ZnS.Cu crystals arise from the quantum mechanical tunnelling through the barrier. Out of phase a.c. electroluminescence arises from the presence of both shallow and deep donors in this phosphor. The experimental voltage dependence of brightness of this component of electroluminescence arises from the relatively continuous distribution in energy of the donor levels and is fairly insensitive to the exact form of the distribution.

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DISCUSSION

Dr. G. F. Alfrey: Mr. Taylor and I have investigated the electroluminescence of single crystals of zinc sulphide. The results differ somewhat from those reported by Dr. Williams, and suggest a slightly different mechanism. Measurements have been made with alternating voltages and the results quoted are independent of the electrodes. The effect of changing from electrodes evaporated on to the crystal surface to electrodes making no contact with the crystal at all is merely to alter the light output by a numerical factor.

Fig. 1 shows the logarithm of the light output as a function of $1/\sqrt{V}$ (V is the applied voltage) at a frequency of 50 c/s and at various fixed temperatures. There is, in our opinion, theoretical justification for putting the results in this form, and the experimental points lie on straight lines. The results

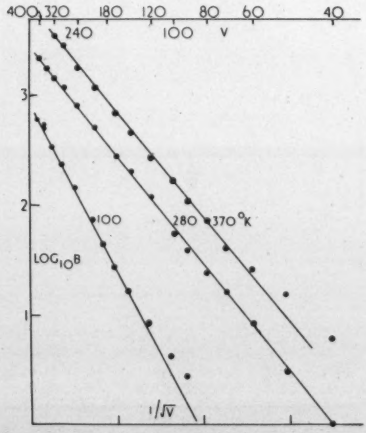

Fig. 1. Log of electroluminescence output at 50 c/s *versus* (voltage)$^{-\frac{1}{2}}$ at different temperatures for ZnS.Cu crystal

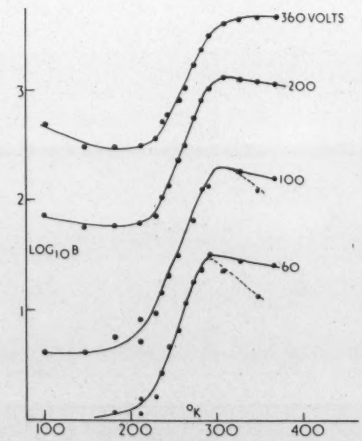

Fig. 2. Log of electroluminescence output at 50 c/s *versus* temperature at different voltages

of Piper and Williams, as well as those given by Destriau,[1] when replotted on this basis, also give straight lines.

Increase of temperature increases the light output, but the slope of the lines in Fig. 1 only changes by 50% for a four-fold temperature increase. These results are more interesting if the light output at various constant voltages is plotted against temperature, as shown in Fig. 2. The light is virtually independent of temperature at low temperatures and again at high temperatures, or it may then even decrease, for the results are somewhat inconsistent in this region. The effect of increasing the voltage is to shift the curve parallel to the light axis without other appreciable changes.

These results can be explained if it is assumed that the luminescence is due to impact excitation of centres, and the increase in light output with temperature is due to excitation by electrons accelerated by the field after thermal ejection from traps. Electrons will be accelerated in this way by a field of frequency ν if the condition $2\nu \simeq s \exp(-E/kT)$ is satisfied, where s, E are constants familiar in glow curve analysis. If ν is increased, the relation can only be satisfied at higher temperatures.

Fig. 3 shows results at 50 c/s and 500 c/s at the same voltage. A marked shift of the curve to higher temperatures is observed at 500 c/s, as suggested above.

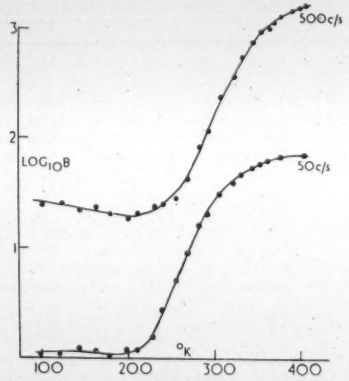

Fig. 3. Log of electroluminescence output *versus* temperature at 50 c/s and 500 c/s. $V \simeq 45$ volts

For clarity, the light output at 500 c/s has been multiplied by 10 and as measured the curves intersect twice over the temperature range employed. This indicates that the result of altering the frequency is likely to be ambiguous unless the measurements can be related to the curves showing the variation with temperature.

Mr. J. B. Taylor: The relations suggested between light output and applied voltage are derived by the use of an efficiency function of the form:

$$\eta \simeq \text{const}\,(E_c^2 - E_i^2)$$

[Equation (1c)].

As pointed out by the authors this function is not strictly correct, and a more reasonable function of the form

$$\eta \simeq \exp(-\alpha/E_c) \qquad (1)$$

can be derived by the simple assumption that collision time is independent of electron energy.

If we insert this into the authors' expression for light output it becomes

$$\phi \simeq \int_0^{E_0} \frac{(E_0 - E_c)}{E_c^{1\cdot2}} \cdot \eta_{(E_c^{1\cdot2})} \cdot \exp(-\alpha/E_c)\,.\,dE_c$$

An approximation to this integral, valid if $\alpha/E_0 > 1$, gives

$$\phi \simeq V_0^{1\cdot4}\eta_{(V_0^{1\cdot4})} \exp(-\alpha/V_0^{1\cdot2})$$

and in general this reduces to $\phi \simeq V_0^n \exp(-\alpha/V_0^{1\cdot2})$, where n is determined by the trap distribution. The value $n = 1$ gives excellent agreement with the data in the paper, as shown in Fig. 4.

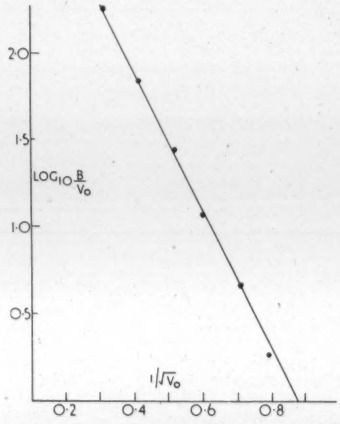

Fig. 4. Piper and Williams' data (Fig. 6) replotted as $\log_{10}(B/V_0)$ *versus* $1/\sqrt{V_0}$

Despite this agreement a different theory, while still accounting for this voltage dependence, will also account for the striking temperature effects obtained by Alfrey and myself.

We have so far assumed that field ionization provides the mechanism for releasing the electrons responsible for electroluminescence, but, in addition, thermal excitation of trapped electrons cannot be neglected.

Assume that a potential barrier is set up near the crystal surface, which will rise and fall during each cycle. As soon as the barrier starts to rise, all electrons which are thermally excited into the conduction band will be accelerated by the field in the barrier and may produce luminescence.

At a time t after the cycle starts, the number of electrons coming from the traps of depth E will be

$$\eta_0\gamma \exp(-\gamma t), \text{ where } \gamma = s \exp(-E/kT)$$

These electrons experience a field proportional to $\sqrt{(V_0 \sin \omega t)}$, so that assuming equation (1) above, this gives as the instantaneous light output

$$B \simeq \gamma \exp(-\gamma t) \exp[-\alpha/(V_0 \sin \omega t)^{1/2}]$$

and hence a total light output per cycle

$$B \simeq \int_0^{\pi/\omega} \gamma \exp(-\gamma t) \exp[-\alpha/(V_0 \sin \omega t)^{1/2}]dt \qquad (2)$$

Provided that $\gamma V_0/\alpha\omega > 1$, this can be reduced approximately to give

$$B \simeq \gamma \exp(-\gamma\pi/2\omega) \exp(-\alpha/V_0^{1/2})$$

This again gives a linear relation between $\log B$ and $1/\sqrt{V}$ which agrees with the results of Piper and Williams, and of Alfrey and myself.

The temperature dependence is the most interesting feature, and for constant V_0 this is given by $B \simeq \gamma \exp(-\gamma\pi/2\omega)$. This expression rises to a maximum given by

$$E/kT_{max} = \log(\pi s/2\omega)$$

which shows how the maximum moves to higher temperatures as the frequency increases, in agreement with experiment.

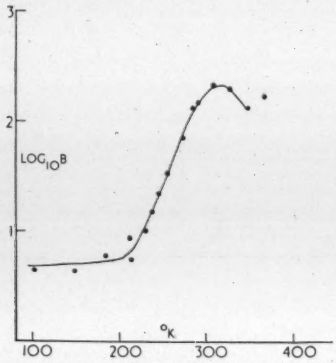

Fig. 5. Agreement of theory and experiment for electroluminescence output *versus* temperature at 50 c/s and 100 V

Points are experimental values. Full line is theoretical for $E = 0{\cdot}3$ eV and $s \simeq 10^7$ sec^{-1}.

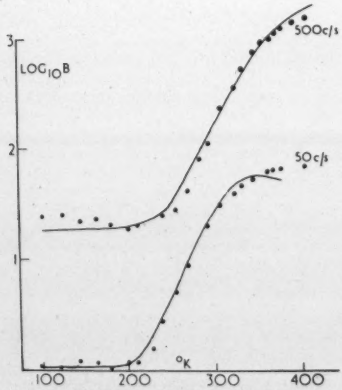

Fig. 6. Agreement of theory and experiment for electroluminescence output *versus* temperature at 50 c/s (lower curve) and 500 c/s (upper curve), and 45 V

Points are experimental values. Full lines are theoretical for $E = 0{\cdot}3$ eV and $s \simeq 5 \times 10^6$ sec^{-1}.

It is well known from glow-curve experiments that there are traps at a depth of approximately 0·3 eV in zinc sulphide, and by using this value of E in equation (2) it is possible to obtain good agreement between theory and experiment, as shown in Figs. 5 and 6.

This agreement suggests that, at least in zinc sulphide, the electrons responsible for electroluminescence can have the same origin as those responsible, under different conditions, for the well-known glow curves.

Dr. G. F. J. Garlick: It seems to be assumed in the paper that the Fermi level is only about 0·5 eV below the conduction band, but this is incompatible with experimental data for zinc sulphide phosphors.

Dr. H. A. Klasens: The authors assume the presence of a large number of donors in the phosphor which are required to build up the exhaustion barrier. This would imply a rather high Fermi level. However, most electroluminescent powders have normally empty traps of considerable depth, as shown by their glow curves. Moreover, ZnS.Cu containing cobalt, which causes a trap level of about 0·5 eV below the bottom of the conduction band, can easily be made electroluminescent, for example, by depositing a copper sulphide layer on the surface of the crystals. Thus in these phosphors the Fermi level must be below 0·5 eV.

Dr. D. Curie: The mechanism described agrees, at least on the main points, with the theories developed by Prof. Destriau and myself. The interesting question is the relative importance of the cathode potential barrier. Electroluminescence is a volume effect, but if the internal field is only great enough in the barrier, light will appear only near to the latter. For a field of 10^4 V/cm in the crystal, the pre-breakdown avalanches, with ionization of the valency electrons, have zero probability but the theoretical acceleration conditions in the theory of dielectric breakdown seem to show that accelerated electrons in the crystal may cause excitation of the centres. For a given sulphide, light may appear only at the surface for threshold fields, but at higher voltages may appear in the bulk crystal; it would also depend on the conductivity of the dielectric in which the sulphide is embedded. In both cases the cathode layer will play a fundamental part in the supply of electrons to the conduction band. The effect, even if appearing only on the surface, seems to be fundamentally different from other surface effects, for instance the emission of light by silicon carbide crystals or in anodic luminescence, as shown by the phase shift of the brightness waveforms and absence of appreciable current through the crystal.

Dr. K. H. Butler: One of the five major hypotheses of the paper is that an exhaustion barrier is formed at the cathode-crystal contact. This immediately limits the possible validity of the theory to single crystals.

It does not seem reasonable to discard the hypothesis of direct field excitation of centres merely on account of approximate estimates of the fields required. The fields present in the proposed exhaustion layer are also unknown.

Calculations by Waymouth show that the direct field excitation mechanism will also lead to a square law relation between brightness and voltage if the density of centres at the surface varies as the 3/2 power of the distance from the surface.

Watson of the Sylvania laboratories has found that pulsed d.c. excitation gives light at both anode and cathode. Moreover, there are frequently potential barriers within the crystal at which luminescence is found.

Although the final equations used in this paper have only two variable constants, this simplicity was obtained by a prior

selection of models, so that the basic theory has many more variables. Hence it seems that agreement of six points (Fig. 6 of the paper) is not sufficient proof that only the theory proposed is valid.

Dr. G. Diemer: It is agreed that in the usual electroluminescent zinc sulphide phosphors most of the potential fall occurs near the cathode. Further support comes from the fact that electroluminescence in zinc sulphide is not stimulated by ultra-violet radiation or X-rays. The following experimental results apparently contradict the above ideas.

The dark resistance of electroluminescent zinc sulphide is rather high, giving for a.c. fields a loss tangent less than unity at audio frequencies.[2,3,4] However, in a fraction of a cycle the large barrier capacitances can be charged and discharged in spite of the large resistance, which suggests that the crystal volume is not ohmic in behaviour for charges injected from the surface. For threshold fields ($\sim 10^4$ V/cm) and a bulk mobility of 250 cm^2 per volt per sec the drift velocity is $2{\cdot}5 \times 10^6$ cm/sec and for a 10 μ thickness the transit time is $0{\cdot}4 \times 10^{-10}$ sec. Thus the conduction electron energy distribution is disturbed and injected electrons pass through the crystal in a very short in-phase transient of current during the first or first few cycles, leaving the crystal through the other barrier in the forward direction. Non-linearity is shown in the voltage-current relations of Fig. 7.[3,4] The shortness of the current pulse relative to the field period gives a small average loss angle over the cycle.

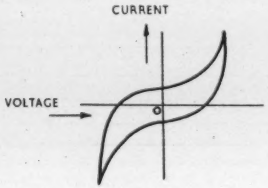

Fig. 7. Current-voltage characteristic for binderless ZnS layer

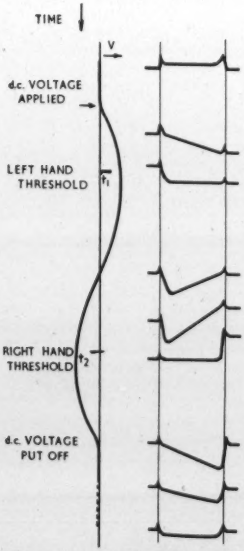

Fig. 8. Variation of field distribution with time across electroluminescent layer

The authors' assumption of a sinusoidal plus d.c. component for the voltage waveform is not to be expected, but a succession of field distributions as in Fig. 8. Between times t_1 and t_2 the voltage across the barrier, which is biased in the reverse direction, can change only very slowly through its own leakage and through the high series resistance of the bulk, which has again assumed its normal dark value as soon as the current flash has passed through it. These barrier voltage waveforms are important in the voltage and frequency dependence of electroluminescence.

Since the current injected is the same for any audio cycle the apparent conductivity of the bulk will increase linearly with frequency, and so the loss angle at high fields will not depend greatly on frequency, as confirmed by recent measurements up to 10^5 c/s.

Rose has shown that when electrons are injected into semiconductors containing traps, the field distribution is distorted by their space charge. Probably also with electroluminescence this space charge plays some role. Indications can be found from the light waveform occurring with a square voltage pulse on a binderless single grain layer (Fig. 9).[3,4] After a

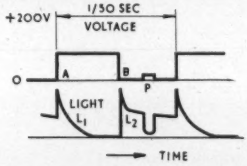

Fig. 9. Light waveforms for square voltage pulses

very sharp excitation at A a light flash occurs with a decay characteristic of ionized centres. The electrons that give rise to this flash L_1 must have been trapped near the centres. That the centres are indeed ionized with electroluminescence can be seen from the flash L_2, occurring after the external field has become zero, and due to electrons that in the strong internal field (that was thus far present) were drawn far away from centres from which they originated, and which are able to recombine as the barrier field gradually decreases through leakage. This recombination giving rise to L_2 can be temporarily suppressed by a very small voltage pulse P. (The theory, of course, needs to be made more quantitative.)

Using Franz's theory of field ionization of donors[5] one finds, contrary to Taylor's assumption, that in the strong fields existing in the surface barrier, tunnelling from non-excited donor levels will be much more likely than thermal liberation.

As regards the donor depths, a lower limit can be found from a.c. conductance, and an upper limit from the fact that the depth may not greatly exceed the separation of activator levels and the valency band, otherwise due to the strong electric fields in the barrier the holes would migrate as soon as they were activated, with quenching of the electroluminescence.[6]

Dr. P. Zalm: From the theory proposed a complete exhaustion of the donors of a given depth in the barrier region appears to be necessary for a linear frequency dependence (over a limited range of frequencies).

Numerical calculations of the rate of tunnelling from localized states as given by Franz[7] lead to the conclusion that the donors are not exhausted at all unless either the field is very strong or the donors are very shallow.

Assuming that in a half cycle of the applied a.c. the donors are not exhausted at all, we might ascribe the voltage dependence of the luminescence to the voltage dependence of the rate of tunnelling. This will give $L \simeq (V + V_0) \exp\left[-b/(V + V_0)^{\frac{1}{2}}\right]$, where L = light output, V = applied voltage, V_0 = constant ($\simeq 2{\cdot}2$ V). This formula fits the experiments over the whole range, L varying by a factor of nearly 10^8. The linear increase of L with frequency is explained by the strong non-linear resistance of the crystal bulk, which gives rise to nearly square d.c. pulses over the barrier (see Fig. 10). After the maximum at A the field decays very slowly because the barrier is biased in the reverse direc-

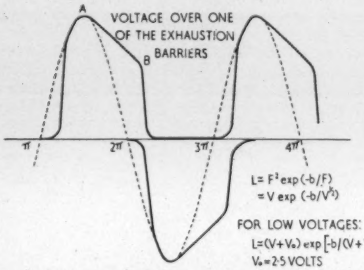

Fig. 10. Comparison of applied and exhaustion barrier voltage waveforms

tion and the bulk is mainly non-conducting. Due to the strong voltage dependence of the rate of tunnelling the greater part of the light excitation takes place very near the maximum of the voltage over the barrier A. This theory has the advantage that no hypothesis about peculiar donor distributions is necessary, and the rate of tunnelling assumed is in accordance with quantum mechanical calculations.

A second comment concerns the authors' assumption of direct excitation of the luminescence centres. For a phosphor with both green and blue copper centres this would give rise to a change in the spectral distribution with voltage, since the energy required to excite a blue centre is larger than that for a green centre. No such voltage dependence has been observed and it seems more likely that excitation occurs in the lattice. The manganese-activated electroluminescent phosphor sensitized by copper does sometimes show a voltage-dependent spectral distribution (blue at low voltages, yellow at high voltages), explicable by transport of energy.

Mr. J. B. Taylor: With reference to the contributions by Dr. Diemer and Dr. Zalm, it seems that essentially we disagree only on the temperature at which the dominant mechanism for the escape of electrons changes from field excitation to thermal excitation. The inclusion of V_0 in Zalm's formula would predict light output at zero applied voltage.

Concerning frequency effects, it is necessary to distinguish results on powders from those on single crystals. In powder phosphors the proportion of the applied field which is effective across each phosphor grain must increase as the frequency rises, as a result of capacity effects at grain boundaries; thus conclusions drawn from such experiments are not very reliable.

Authors' reply: The aspect of the mechanism proposed in the extended discussions of Dr. Alfrey and Mr. Taylor which departs most radically from our theory is that the deep donors are emptied thermally rather than by the local field. If thermal ionization of the deep donors dominates, then it is clear that: (*a*) At high temperatures the donors would have such a short time constant for thermal ionization that all of them would be ionized in the presence of a low field and their electrons swept out of the exhaustion barrier before the local field strength was great enough to accelerate them to large kinetic energies. (*b*) At intermediate temperatures the number of occupied donors at the time when sufficiently high fields are attained would depend markedly on how rapidly the field strength varies. This would cause a super-linear dependence of brightness on frequency. Also, the brightness would vary with wave form at constant frequency and peak applied voltage. (*c*) At low temperatures when only a small fraction of the donor levels ionize during the voltage cycle, the brightness would become independent of frequency but still be sensitive to waveform, and would drop off exponentially to zero with decreasing temperature. In marked contrast to these characteristics of a thermally controlled mechanism, experimental data on zinc sulphide show the brightness to vary linearly with frequency (with some saturation at high frequency) over a wide temperature range, and to be independent of the waveform. These data agree with a field-controlled mechanism.

With P. D. Johnson we have also noted a decrease in brightness at low temperatures in both single crystals and powder cells, but in many samples the brightness recovers at still lower temperatures. In single crystals the brightness at 30° K equals the brightness at 300° K. The temperature dependence of electroluminescence can be quantitatively correlated with thermoluminescence data, retaining the idea of field ionization of the deep donors in the exhaustion layer.

In deriving equation (2), Taylor does not account for the variation in field strength as a function of the position in the barrier, although he assumes the barrier model. Such an omission alters the results quite markedly. Furthermore, it is apparent that Taylor's derived expression for brightness does not yield the theoretical curves shown in Figs. 2 and 3 of our paper which he reports were computed from equation (2). Specifically there is no factor to account for the curves flattening out at 200° K instead of continuing towards zero at lower temperatures.

In regard to the Seitz efficiency function appearing in our paper and in equation (1) of Taylor's comments, we have recently substituted this function in our equation (2*b*) and integrated the resulting expression numerically to find close agreement with our earlier approximation.

In reply to the remarks of Dr. Garlick and Dr. Klasens, we believe that it is not necessary that the Fermi level should be very near the conduction band in electroluminescent zinc sulphide. During the first few voltage cycles the deep donors are ionized and from then on the shallow traps can behave essentially as donors.

In reply to the remarks of Dr. Butler, we do not imply that the theory proposed is the only possible interpretation, but it appears to be the mechanism most nearly in accord with the available data. Direct field ionization of the activator system requires at least fifteen times the local field necessary to ionize donors of suitable depth for our mechanism.

In reply to Dr. Diemer and Dr. Zalm, we would like to re-emphasize that in our mechanism the field distribution in the crystal is controlled by shallow donors. While these donors can be field excited, they are more easily ionized thermally at most temperatures. Thus, the strong field necessary to ionize deep donors which provide the conduction electrons in the high field region is created by the positive space charge in the Mott–Schottky barrier which has been exhausted of electrons from the shallow donors. We have neglected the further increase in space charge accompanying the ionization of deep donors.

Diemer's and Zalm's statements suggest a mechanism utilizing only deep donors which are field ionized at quite a slow rate. While this mechanism is attractive because of its simplicity, it cannot account for the linear variation of light output with frequency, or for the independence of the integrated light output of the change in voltage waveform.

With reference to Diemer's comments on the dielectric properties of electroluminescent zinc sulphide, our proposed mechanism corresponds more closely to a resistor and capacitor in series than to any other simple electrical analogue, and it is evident that this is not in disagreement with the properties quoted by Diemer. A low bulk resistivity and our mechanism leads to a small loss tangent as reported. It is not surprising that the barrier capacities are easily charged and discharged on the basis of this mechanism. A loss angle independent of frequency is not unexpected if the bulk resistivity is sufficiently low.

Diemer apparently proposes a low bulk conductivity with no shallow donors; otherwise the potential energy distributions shown in Fig. 2 of our paper would not be possible. However, he mentions a threshold field of 10^4 V/cm which agrees with the average fields measured by Roberts in powder samples. Using Franz's field ionization formula, a field of 10^4 V/cm cannot ionize donors more than 0·1 eV deep. But such donors with a frequency factor as low as 10^8 sec^{-1} are thermally ionized in less than 10^{-6} sec. If one considers, as Zalm does, deeper donors which are thermally stable and are field-ionized at quite a slow rate, then Diemer's potential distribution, shown in Fig. 2 of our paper, should be replaced by a uniform field proportional to the applied voltage. Since Zalm assumes that most of the donors are still full throughout the voltage cycle, the average light output would remain constant, independent of a change in frequency, but sensitive to the shape of the voltage cycle (experiments indicate no change in light output when pulses of constant voltage and repetition rate are varied in duration from 100 to less than 1% of the cycle time). It is astonishing that Zalm attempts to account for a linear frequency dependence of brightness by means of a non-linear bulk resistivity.

Zalm is incorrect in concluding that our mechanism requires a peculiar donor distribution. Rather we have shown that agreement with experiment is quite insensitive to the detailed donor distribution. He has also failed to appreciate that in this mechanism the local field configuration at the time a donor empties is independent of peak applied voltage. Thus, the invariance of the relative intensities of different emission bands with applied voltage would not resolve the alternative possibilities we pointed out, namely, of impact excitation or ionization of the activator centres, or impact ionization of the lattice.

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(6) This Supplement: see Fig. 2 in discussion of Paper 8.
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Paper 8

Brightness waveforms in electroluminescence

By Prof. G. Destriau,* Laboratoire de Luminescence, Faculté des Sciences de Paris

The shape of the "brightness waves" in electroluminescence depends on many factors: field intensity, frequency, and the direction in which the light output is observed. The shape also depends on the device used as electroluminescent condenser and, for some substances, the shape is slightly different according to the spectral region observed. In the Gudden and Pohl effect (momentary illumination) there is a similar appearance of the disturbances shown in electroluminescence. In the electro-extinctive effect the shape of the brightness waves changes quickly during the first second and then slowly for about ten seconds after the field is applied.

The term "brightness waves" is applied to the curves which give the light emission as a function of time during a cycle of variation of the potential applied to an electroluminescent condenser. The fact that the light output varies with twice the applied frequency was reported in 1937,(1) and further data given in 1938.(2) Brightness waves were originally obtained by a rotating disk method,(3) but now by the use of a photomultiplier and oscilloscope.

THE SHAPE OF THE BRIGHTNESS WAVE

This shape is not symmetrical when stimulated by a sinusoidal field, but the two maxima per cycle are unequal and, furthermore, the slope of the curve differs according to whether the brightness is increasing or decreasing. Usually one of the appearances shown in Fig. 1 is obtained. For some samples the highest peak occurs when the conducting glass through which we observe is negative, for others when it is positive. This difference between the heights of successive peaks may be the consequence of a strong surface emission, in which case the light received by the photomultiplier is different for the two surfaces alternately excited.(4) However, the differences in the polarity of the highest peak (see Fig. 1) are not always in good agreement with this hypothesis.

If symmetrical cells are used, for example with two conducting glasses, the shape of the brightness waves is greatly simplified. The highest level now occurs when the electrode

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through which we observe is negative (Fig. 2), which seems to disprove the suggestion that electroluminescence is a surface phenomenon. The small difference between the peaks observed for a symmetrical cell may perhaps be the consequence of an optical effect unconnected with electroluminescence. An experiment supporting this idea was the illumination of a photomultiplier through a transparent symmetrical condenser without a phosphor; an alternating potential applied to the electrodes caused a very slight modulation of the light falling on the photomultiplier, and at twice the applied frequency, as though the transparency of the insulator was modified by the field.

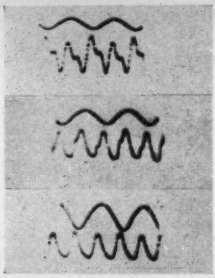

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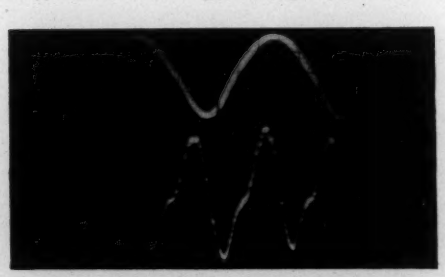
Fig. 1. Simultaneous recordings of sinusoidal potential wave and brightness wave from nonsymmetrical cell (conducting glass and aluminium backing)

(*a*) ZnS . Cu with inflexion on decreasing side, highest peak with Al^+.
(*b*) ZnS . Pb with inflexion on increasing side, highest peak with Al^-.
(*c*) ZnS . Mn with more regular wave, highest peak with Al^+.



(*a*)

(*b*)

Fig. 2. Brightness waves for ZnS . Pb

(*a*) nonsymmetrical cell.
(*b*) symmetrical cell.

All experiments described below were done with nonsymmetrical cells with conducting glass as the transparent electrode and aluminium as the metal backing for the second electrode. The irregularities in the brightness waves obtained with such cells may be due to asymmetry of the internal field resulting from the Lilienfeld effect (emission of electrons from the metal in strong fields). This would produce stronger light emission near one of the two electrodes and so give the appearance of surface emission.

To summarize, it is considered that electroluminescence is a volume effect, but as the field is stronger near one of the faces, the light output is also greater near the same face.[5]

VARIATIONS IN THE SHAPE OF THE BRIGHTNESS WAVE WITH FREQUENCY

The brightness waves are not in phase with the applied field. Having regard to the small conductivity of the crystal, the internal field leads the applied potential by an angle ϕ_1, where

$$\tan \phi_1 = 2/\epsilon\rho\nu$$

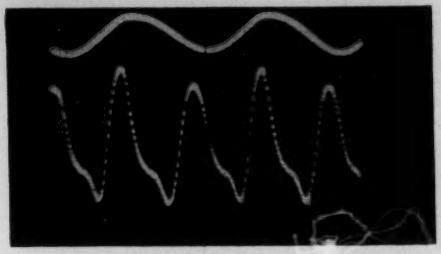
and ϵ is the dielectric constant, ρ the resistivity, and ν the frequency. It is clear that the brightness waves must lead by the same angle if the time of decay of electroluminescence is very short compared with the period T of the applied field. When the frequency rises, evidently ϕ_1 decreases, but the corresponding angle of lead ϕ_2 for the brightness waves decreases even more than ϕ_1 since the decay time of the luminescence cannot be neglected at above 1000 c/s. The brightness waves then lag the internal field; above 1000 c/s ϕ_2 may become negative so that the waves also lag the applied potential. These effects are shown in Fig. 3.

The waveforms are simplified and more symmetrical at higher frequencies, in accordance with expectation since the time during which the Lilienfeld emission can occur is reduced. The field distribution thus becomes more uniform. When a constant field is applied the internal field decays exponentially[6] with time constant θ_1 where $\theta_1 = \epsilon\rho/4\pi = 1/2\pi\nu \tan \phi_1$. To determine the decay time at low frequencies, the electroluminescence cell may be subjected to a constant field, which results in a high instantaneous light emission and an exponential decay of time constant θ_2. If the electroluminescent decay is short $\theta_1 \simeq \theta_2$, and assuming $\phi_1 = \phi_2$ at low frequencies, then $\theta_2 = \dfrac{1}{2\pi\nu \tan \phi_2}$, which is in good agreement with experiment below 200 c/s. However, no relation has been determined between θ_2 and the values of ϕ_2 found at high frequencies.

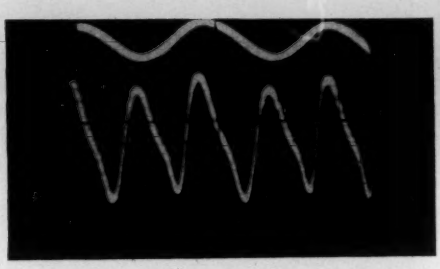
VARIATIONS IN THE SHAPE OF THE BRIGHTNESS WAVE WITH SPECTRAL REGION

In an electroluminescent phosphor with two activators, each is responsible for the emission of one spectral band: for example, ZnS . Mn, Cu gives in electroluminescence the yellow Mn band and the blue Cu band, but these bands are

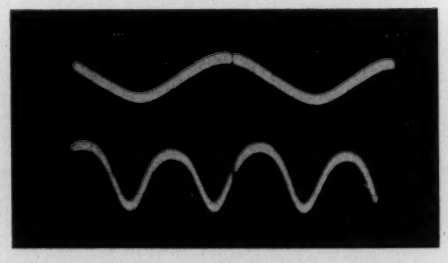
not emitted simultaneously so that they have different phase angles ϕ. In this case we obtain a different shape if the light passes through different coloured filters before falling on the photomultiplier.



(*a*)



(*b*)



(*c*)

Fig. 3. Brightness waves for the same field at (*a*) 60, (*b*) 600, and (*c*) 4500 c/s.

In other samples with only one activator there are differences according to the spectral region observed, but all electroluminescent products do not show this effect. It is possible that the various spectral regions of a single band are not emitted simultaneously; the appearances suggest that the longer wavelengths are delayed in time compared with the shorter wavelengths.

Since ϕ varies, $\epsilon\rho$ is not constant, but increases with increase of wavelength in the neighbourhood of the emitting spot in the crystal.

VARIATIONS IN THE SHAPE OF THE BRIGHTNESS WAVEFORM WITH FIELD INTENSITY

Lastly, the shape of the wave changes with the field intensity. A small increase of ϕ occurs when the intensity increases;[3] this is a consequence of the increase of conductivity of semi-conductors under the action of high fields. There are also large changes in the waveform, chiefly on the disturbed side of the waves. For some samples, when the field intensity increases, a secondary maximum appears instead of the inflexion (Fig. 4), and this new maximum is

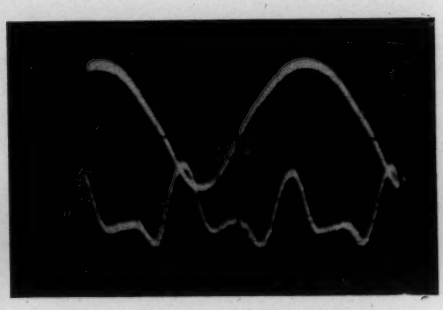


Fig. 4. Brightness waves at high field intensity. Compare with Figs. 1(*a*) and 3(*a*) for low field intensity

located in the cycle at about the time when the field is zero. With still greater field intensities this secondary maximum becomes less important. Other authors, using a single crystal, have found a similar secondary maximum.[7]

THE BRIGHTNESS WAVEFORM IN THE GUDDEN AND POHL EFFECT

This effect is the momentary illumination which occurs when ZnS of long afterglow, previously stimulated by X-rays or ultra-violet radiation, is submitted to an electric field. Waveforms have been given elsewhere.[8] Some of the effects are similar to those described for electroluminescence. Thus in one sample of ZnS.Cu the brightness peak was found to lead the potential peak at 50 c/s, but to lag at 1800 c/s. Fig. 5 shows a directional effect.

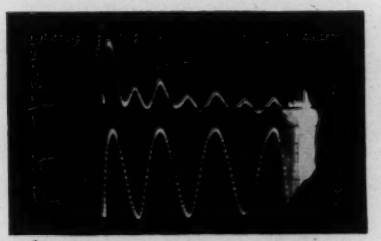
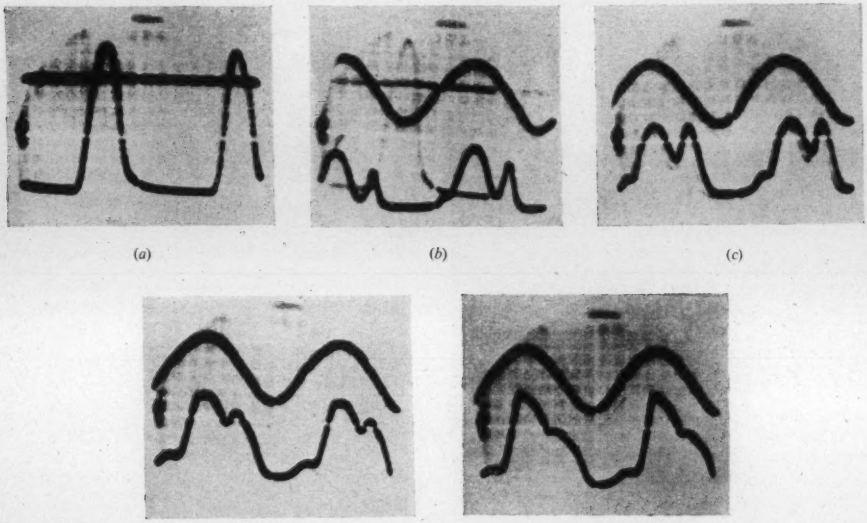


Fig. 5. Gudden and Pohl effect in ZnS (prepared by Prof. Guntz). The odd peaks are higher than the even

THE BRIGHTNESS WAVEFORM IN THE QUENCHING OF LUMINESCENCE

When ZnS or CdS of short persistence is subjected to X-rays or ultra-violet radiation, the sensitivity of the phosphor is, in general, weakened by the additional action of an electric field.[9-12] If the phosphor is subjected to X-rays, the application of the field is followed by strong quenching during which the brightness waves are greatly modified by the appearance of a sharp maximum when the field passes through zero. The amplitude of this maximum varies rapidly during the cycles which immediately follow application of the field. Fig. 6 shows some of the appearances produced with a successive half cycle. There is thus gradually established, under the action of the varying field, a statistical distribution of the electrons so that those which have been displaced too far cannot return until a certain time has elapsed; this may be even more than a second. In this distribution, even when the equilibrium region has been reached, there is always a small number of electrons remaining in the neighbourhood of their respective centres which have a tendency to return each time the field falls to zero. Consequently there is a residual deformation of the brightness waves even during the equilibrium state. When the field is completely removed, all the electrons return gradually to their original levels and the



(*a*) (*b*) (*c*)

(*d*) (*e*)

Fig. 6. Quenching by electric fields. Upper trace in each is sinusoidal field

(*a*) brightness wave with no field. Disturbances of brightness waves.
(*b*) immediately after field is applied.
(*c*) 0·18 to 0·20 sec after application of field.
(*d*) 0·90 to 0·92 sec after application of field.
(*e*) 3·78 to 3·80 sec after application of field.

half-wave X-ray generator. On application of the field the average brightness of the screen falls to a very low level and then rises towards a limit; simultaneously the brightness waves change towards a permanent form different from those obtained when no field is acting.

The secondary maximum and its variations indicate in another way the inner disturbances caused by the field in the statistical equilibrium of electrons in the lattice. The temporarily displaced electrons return to their original positions as soon as the field falls to zero and produce the emission in this sharp secondary maximum; but it is quite certain that the perturbations caused by the field are not instantaneous. Of the electrons momentarily displaced when the field is a maximum, only a certain number return to their original levels when the field falls to zero; the others, which have been more effectively displaced, have a smaller probability of return and are progressively displaced still further with each brightness waves resume their normal form with gradually increasing amplitude.

As in normal electroluminescence, the brightness waves take a different form if the light passes through a coloured filter.

CONCLUSIONS

The brightness waves provide a useful method for studying the mechanism of electroluminescence and that of other similar effects.

It is considered that electroluminescence is a volume effect but with a greater emission near the surface because the field distribution is disturbed by a strong Lilienfeld emission.

At high frequencies the time of decay cannot be neglected in comparison with the period of the sinusoidal field, and then the brightness waves are shifted behind the field. The same behaviour occurs in the Gudden and Pohl effect. In

the quenching of luminescence by alternating fields the brightness waves change during a fraction of a second following the field application. These disturbances demonstrate the action of the field on the inner statistical equilibrium of electrons between the different levels of the crystal lattice.

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DISCUSSION

Dr. P. Zalm: Prof. Destriau believes that the unequal light peaks observed with symmetrical cells disprove the assumption that electroluminescence is related to a surface phenomenon, and are due to an optical effect. The inequality has, however, been found to decrease with increasing thickness of the cell, as would be the case if each crystal emits light on the side towards the cathode.[1, 2] Destriau's explanation would require increasing inequality of peaks with increasing thickness.

Other proofs that the light is emitted from a very small region of the grains are:

(*a*) Stroboscopic experiments, also mentioned by Butler.

(*b*) Glow experiments, showing that during electroluminescence the traps are neither filled nor emptied.

(*c*) Sensitization of electroluminescence by surface treatment with a second phase of polysulphides of Ca, Ag, Au, alkali metals or alkaline earth metals.

(*d*) Electroluminescence of the powders described in (*c*) cannot be stimulated by ultra-violet radiation or X-rays.

Dr. G. Diemer: In his experiments using X-ray excitation plus an a.c. field, Prof. Destriau has given evidence for delayed emission in the electric field: the field gives rise to a spatial separation of the electrons and the centres from which they originate. This effect also plays a part in electroluminescence where a strongly non-uniform excitation of the crystal occurs, as is the case with X-ray excitation.* This is seen from Fig. 1, where an oscillogram is given for a binderless single grain layer under d.c. excitation, using pulses of a

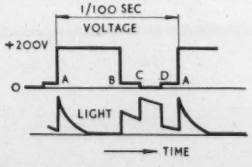

Fig. 1. Electroluminescence under d.c. pulse excitation

particular shape at 100 c/s. At *A*, a short light flash occurs as with a.c. square wave excitation. Furthermore a slowly decaying flash is observed at *B*, when the external field is reduced to near zero. This recombination flash is due to migration of the electrons to the centres while the internal field decays slowly. The light rises to a much higher level when the external field becomes exactly zero (point *C*).

It is believed that the secondary peaks, often occurring with sinusoidal operation at the moment when the applied voltage goes through zero, are due to this delayed emission.

Since with electroluminescence most of the emission is delayed owing to the presence of the electric field, radiationless processes will be enhanced due to hole migration. This so-called field quenching of luminescence is a reason for the low efficiency. That the hole migration is indeed stimulated is clearly seen from the measured temperature dependence

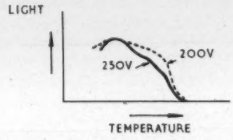

Fig. 2. Temperature dependence of electroluminescence at different voltages

(Fig. 2). At higher voltages the quenching sets in at a lower temperature.

Mr. A. N. Ince: Recent papers on electroluminescence by Destriau and Curie have assumed that the local and mean macroscopic fields are the same and equal to 40 000 V/cm, hence the mean free path, in the field direction, of electrons which excite the luminescence centres should be about 5×10^{-5} cm or more. One would therefore expect, as suggested by Destriau, that the application of a magnetic field of the order of 100 000 oersteds, perpendicular to the electric field, would lead to decrease of the emitted light. I have carried out this experiment with a green emitting powder phosphor using a field of 130 000 oersteds, but found no effect. This may be explained either because (*a*) the field-accelerated charges have greater mass than that of electrons (ion excitation), or (*b*) electrons have a shorter path and consequently the local field is greater than the mean macroscopic field.

It is difficult to accept the first possibility, but for the second one it may be assumed that a high local field exists in the boundaries of the powder grains, not due to a volume electronic polarization. This agrees with the cathode-barrier mechanism proposed by Piper and Williams for single crystals making direct contact with electrodes. Although in the case of powder phosphors the grains are embedded in a dielectric medium, each grain may still have, as it were, its own electrodes in the form of a metal coating, as suggested by Kröger.[3]

This possibility indicates that the mechanism of electroluminescence in single crystals and powder phosphors is similar, in spite of the doubts expressed by others.

* See references 3 and 4 in discussion of Paper 7.

The importance attached to the shape of brightness waveforms as intrinsic properties of phosphors is not justified, unless the harmonic content in the applied voltage is quite low. In some slides shown by Prof. Destriau for the same phosphor at different frequencies, there was a sort of random relationship between the heights of the adjacent brightness wave peaks and in some cases the tops of the curves were flattened as though by saturation of the oscilloscope amplifier.

In my slides were seen two brightness waves corresponding to emissions viewed from two sides of a symmetrical cell with two transparent electrodes. The two waves were in phase, i.e. smaller and greater peaks of the brightness waves were emitted simultaneously from both sides of the cell. For a second harmonic content of 6% the difference in height of neighbouring peaks was 40%, whereas for 0·3% content this difference was negligibly small. From my slides of green and blue emission waveforms of a green-blue phosphor it is possible to locate the part of the cycle where green centres are mainly excited as corresponding to decreasing applied voltage.

Author's reply: In reply to Dr. Zalm, if electroluminescence was a pure surface effect, the highest peak should always occur for the same polarity, but this is not so. Even for the same sample this polarity changes when the applied voltage is increased. On the other hand, electroluminescent crystals show many luminous spots under the microscope, some near the surface but others in the body of the crystal.

In reply to Dr. Diemer, the secondary peak of the brightness wave, or the inflexion, may occur either on the increasing or the decreasing side according to the applied voltage. This change in position of the secondary peak is independent of the metal backing, for which we have used Cu, Ag, Au, Pb, W, Al, Fe, Pd and In.

With regard to Mr. Ince's comments, some experiments of D. Curie have shown that when electrodes are in contact with a crystal, the pure electroluminescence is complicated by secondary effects.

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Paper 9

Electroluminescence of organic compounds

By Prof. A. BERNANOSE, Faculté de Pharmacie, Université de Nancy, France

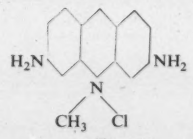
Electroluminescence has been produced in organic fluorescent compounds. Adsorbates of such materials on cellulose films have been prepared which when dry and free from oxygen show phosphorescence. The films are mounted as the dielectric of a condenser having one transparent electrode and an alternating potential is applied. After these dielectric cells have been exposed to sunlight they show an electrophotoluminescence which quickly disappears leaving the normal electroluminescence. New emission bands in addition to the normal bands of luminescence emission are observed. Compounds investigated include gonacrin, brilliant acridine orange E and carbazole.

Since inorganic phosphors become luminescent under the sole action of intense alternating electric fields we have attempted to obtain the same phenomenon for adsorbates of organic molecules. When the latter are dispersed in a rigid medium they can exhibit phosphorescence. For dispersion in cellulose films the latter must be very dry and oxygen must be eliminated. After some preliminary difficulties we have succeeded in using this medium for the study of electroluminescence in organic compounds.

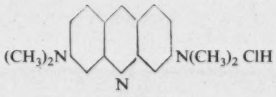
PREPARATION AND MOUNTING OF ELECTROLUMINESCENT CELLS

Earlier methods of making cells and the circuits used for measurement have been described elsewhere.[1] Films of cellophane are plunged into the fluorescent solution, dried, and finally placed with melted paraffin wax between a plate of aluminium and a sheet of mica. The whole is compressed to exclude air bubbles before cooling. The mica sheet is wetted on its exterior surface by a saline glycerine solution. The total thickness of dielectric in the cells is from 0·1 to 0·2 mm. The alternating applied potential was obtained from a mains transformer (50 c/s) and a potential difference of up to 2000 V could be used. The emission was measured by a photomultiplier (either R.C.A. type 1P21 or a Lallemand 18 stage type) as previously described.[2]

Trials were made with acridine derivatives: gonacrin (I) and brilliant acridine orange E (II) at concentrations of 1/25 000 to 1/200 000, and also with carbazole.



(I)



(II)

From preliminary results it appears that other fluorescent compounds may show the effect provided that they do not

introduce appreciable electrical conductivity into the cellophane film.

STUDY OF EMISSION

Variation of brightness with applied potential. The prepared cells only show the electroluminescence effect proper after a certain time has elapsed. Initially two different phenomena occur: a lack of sensitivity due, in our opinion, to the presence of oxygen, and electrophotoluminescence due to release by the applied field of energy which was previously stored during exposure of the cells to daylight. After "aging" of the cells, which consists of exposure to sunlight, application of a field produces relatively strong emission which decays away leaving the normal electroluminescence emission after some hours. After such a procedure the cell shows stable performance. Increase of the applied field is ultimately limited by puncture of the mica and occurrence of discharges around the edges of the cell, the latter being evident from fluctuations in the recording galvanometer. Visual tests reveal that, below the field limit, the emission is due to luminescence in the body of the dielectric and not to spurious discharges.

For a given cell a potential V produces a surface brightness B which follows the relation:

$$B = aV^2 \exp(-b/V) \tag{1}$$

where a and b are constants. This relation is similar to that obtained by Destriau for ZnS phosphor cells.[3]

Oscillographic study of electroluminescence. Cells were prepared as described above and examined by Prof. Destriau and Mme. M. Destriau, using oscillographic methods available in Prof. Curie's laboratory, with field frequencies from 50 to 500 c/s. It was observed[4] that the brightness waveform leads the voltage waveform. Destriau has shown[5] that the real field in the dielectric ξ is related to the applied field E thus:

$$\xi = E \Big/ \left[1 + \left(\frac{4\pi}{\epsilon\rho\omega}\right)\right]^{\frac{1}{2}} \tag{2}$$

where ϵ is the dielectric constant of the medium, ρ the resistivity and ω the angular field frequency. The phase angle of the real field relative to the applied field is given by:

$$\tan\phi = 4\pi/\epsilon\rho\omega \tag{3}$$

We have calculated that for the two frequencies used, $\omega_1 = 100\pi$, $\omega_2 = 1000\pi$, $\tan\phi_1/\tan\phi_2 = 10$.

For our cells, as for ZnS type cells, it is found that the real field determines the electroluminescence as soon as the threshold potential, characteristic of a given cell, is reached. While the brightness follows the field variation at 50 c/s, a weak persistence is observed at 500 c/s between excitation regions. The same cells show a phosphorescence of several seconds duration after exposure to sunlight.

EMISSION SPECTRA

From preliminary trials on acridine orange[6] the emission spectrum appears to be independent of the applied field. However, there was evidence for a new band in the blue region, but no explanation of this is yet available. These first measurements are only approximate being obtained by the use of interference filters.

ELECTROPHOTOLUMINESCENCE

The electrophotoluminescence which perturbs the initial observation of electroluminescence can be studied as follows. The cell is kept in the dark and then illuminated under known conditions, the subsequent variation of emission with time being measured for a given applied potential. Electrophotoluminescence was observed in all cases, but was most noticeable in the case of carbazole. For one of these cells the variation of emission B_1 with time t was determined and is given by:

$$B_1 = B + \alpha \exp(-\beta t) \tag{4}$$

where α and β are constants and B is the normal electroluminescence brightness. α and β depend on the conditions of previous illumination of the cell. For a particularly good cell, exposure to sunlight for several hours was followed by an emission of electrophotoluminescence some 20 times greater than the normal electroluminescence. This enhanced emission decreased to half its initial value in 3 min, normal brightness of electroluminescence being reached in about 20 min.

CONCLUSION

The two phenomena of electrophoto- and electroluminescence are experimentally distinguishable for these organic fluorescent compounds. The emission laws relating brightness to applied field appear to be similar to those found for inorganic phosphors.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the help of Profs. M. Curie and G. Destriau, Mme. M. Destriau, and my collaborators MM. P. Vouaux and G. Marquet.

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DISCUSSION

Dr. D. Curie: Although organic and inorganic materials show similar electroluminescence relations the necessary fields are much higher, and the mean acceleration paths are much smaller for the organic case and correspond to molecular size. The exponential brightness-field law for organic materials may thus be due to a Zener effect, in contrast to the inorganic case where the fields are not high enough.

Dr. P. Zalm: Regarding the experiments of Prof. Bernanose, attention should be directed to the so-called Reboul effect, occurring at the anode side of insulating layers where soft cathode-rays or X-rays can be emitted. These rays can excite any normal non-electroluminescent phosphor.

Author's reply: In reply to Dr. Curie, it is possible that energy transfers occur between organic molecules, or that electrons move into organic crystals, but so far there is little experimental evidence.

Dr. Zalm's suggestion is a possible explanation, though the brightness waves suggest electroluminescence. No work has been done with d.c. fields.

[The following is a summary of a short lecture given during the session on Electroluminescence.]

Dr. G. Szigeti: The electroluminescence of silicon carbide crystals has been reported by several workers,[1-5] together with attempts to provide a theory of the effect. To provide more experimental data to distinguish between the theories we have measured the detailed characteristics of the emission spectrum and its temperature dependence. A microscope-spectrophotometer designed by G. Bauer of our laboratory was used. This gave an accuracy of 15% in intensity measurement and a resolution of approximately 20 Å in wavelength. The spectral distributions for the silicon carbide emission and absorption are given in Fig. 1 which also includes earlier

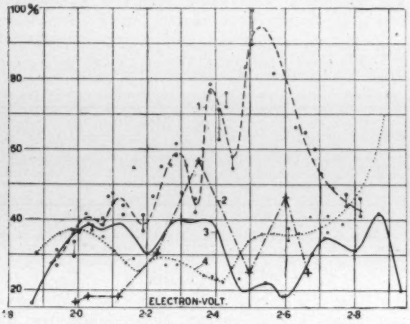

Fig. 1. Spectral distribution of emission and absorption

Curve 1, electroluminescence of silicon carbide.
Curve 2, electroluminescence of silicon carbide.[4]
Curve 3, cathodoluminescence of boron nitride.[5]
Curve 4, absorption of silicon carbide.

results by Lehovec and others.[4] There is marked agreement of maxima with those given in Fig. 1, Curve 3, for the cathodoluminescence of boron nitride containing carbon impurity.[5] The best agreement is for the peaks at 2·025, 2·125, 2·285 and 2·385 eV. From the measured spectra we can derive the energy level scheme of silicon carbide as shown in Fig. 2. It seems probable that excess of carbon in the carbide is responsible for the emission centres since the spectra are not altered by impurities, except adversely in intensity. The activation energies for hole semi-conduction will be 0·15 and 0·25 eV from Fig. 2. Lehovec found 0·12 eV for the

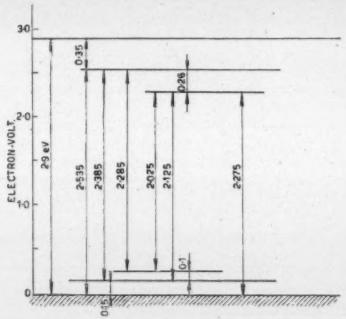

Fig. 2. Energy level scheme for silicon carbide

activation energy involved in the variation of emission with temperature (18–136° C), while Braun and Busch[6] give 0·3 eV and 2·3 eV for the activation energy of semi-conduction at low and high temperatures respectively. Thus reasonable agreement is shown with results from spectral measurements.

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Paper 10

Some experimental results on electroluminescence

By Prof. A. Luyckx, Ir.U.I.Lv., University of Louvain, and A. J. Stokkink, D.Sc., Ateliers de Constructions Electriques de Charleroi

Results are presented on the relation between voltage and the logarithm of light output, which gives a linear plot for ZnS . Mn but not for ZnS . Cu. Irregularities in the brightness waveforms are attributed to imperfections in the applied sinusoidal potential. Work on the electroluminescence of zinc silicate, and on polarity effects, is also mentioned.

LIGHT OUTPUT

Electroluminescent lamps were made by incorporating the phosphors in a hard plastic medium spread on conducting glass, and backed by the second electrode of evaporated metal, metal foil, or conducting varnish. The light output was measured by an R.C.A. 931 photomultiplier at a distance of 4 cm from the luminous capacitor. Fig. 1 shows results for a yellow-emitting phosphor, ZnS.Mn, characterized by a

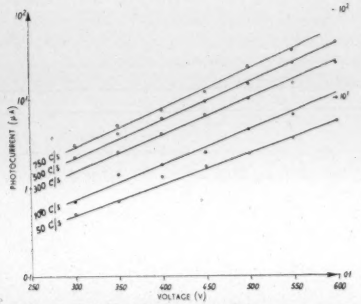

Fig. 1. Logarithm of surface brightness *versus* alternating voltage for ZnS.Mn

linear relation between applied voltage and the logarithm of the photocurrent (the brightness is proportional to the photocurrent). A second ZnS.Mn phosphor gave similar results.

Fig. 2 refers to a green-emitting phosphor, ZnS.Cu, and here the linear relation is not obtained, at any rate over the same voltage range. The rate of rise of brightness with voltage is greater than for ZnS.Mn.

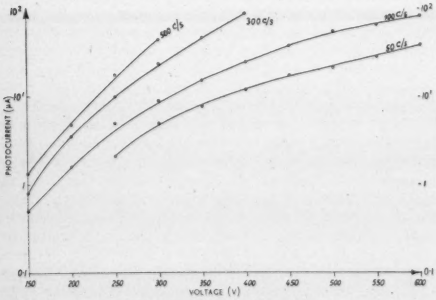

Fig. 2. Logarithm of surface brightness *versus* alternating voltage for ZnS.Cu

BRIGHTNESS WAVES

Destriau* has published results showing inflexions on the waveforms of electroluminescence, these irregularities in the curves being sometimes on the rising, sometimes on the falling side of the wave. Attempts to repeat these experiments showed that the effect was related to certain frequencies and voltages. Slight deformations were visible on the voltage waveforms, and these appeared to affect the brightness waves to an exaggerated degree. Fig. 3 shows two cases observed for ZnS.Cu, together with the undistorted response at a different frequency. This last could be obtained for the same material at any voltage between 50 and 2000 V, and any frequency between 50 and 1000 c/s, when the generator had been readjusted.

(*a*) (*b*) (*c*)

Fig. 3. Potential and brightness waves for ZnS.Cu, showing effects of slight distortions in voltage wave (*a*) 180 V, 100 c/s; (*b*) 180 V, 110 c/s; (*c*) 180 V, 200 c/s.

In general, the brightness waves led the voltage waves slightly at all frequencies up to 1000 c/s for ZnS.Mn. With ZnS.Cu the forward phase difference was much more important than for ZnS . Mn, but it decreased with frequency increase, and nearly disappeared at 500 c/s.

SILICATE ELECTROLUMINESCENCE

Zinc silicate activated by manganese has been found to exhibit electroluminescence under the conditions described. The phase shifts are sometimes leading, sometimes lagging. Fig. 4 shows the brightness waveforms with an unusual

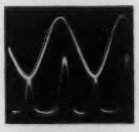

Fig. 4. Potential and brightness waves for Zn_2SiO_4.Mn at 1700 V, 50 c/s

* Destriau, G. *Bull. Soc. Franç. des Elect.*, **3**, p. 381 (1953).

feature, namely the high-frequency components seen to be superimposed on the normal wave; these may be attributed to pre-breakdown phenomena.

POLARITY EFFECTS

In general, peaks of the brightness waves alternate in height. It was found that, according to whether the transparent electrode or the metal electrode was earthed, the higher peaks corresponded to the potential maxima or minima respectively.

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DISCUSSION

Dr. G. Diemer: Slight distortions of the voltage wave may affect the shape of the brightness wave as well as inequality in the peak heights, but there is sufficient evidence* to show that with a perfect sinusoidal voltage wave secondary light peaks may still occur. Also, with thin layers, unequal heights of the main peaks may be observed.

The secondary peaks can be ascribed to the delayed emission in an electric field combined with the action of traps; their occurrence depends on the chemical nature of the phosphor. For instance, zinc sulphide with only traps of small depth does not show secondary peaks at room temperature, but does so at 170° K. When the phosphor contains traps of various depths, the ratio of the height of the secondary peak to that of the main peak can pass through various distinct maxima at different temperatures.

Dr. K. H. Butler: Dr. Waymouth has studied the waveform of light emitted by powder phosphors embedded in dielectrics and viewed through a microscope at right angles to the field; he found symmetrical brightness waves, which we believe to be characteristic of the phosphor rather than of the lamp construction.

Dr. D. Curie: Prof. Destriau's theoretical formula gives a linear relation between $\log B$ and $1/V$, whereas the results for ZnS.Mn show linearity between $\log B$ and V. The data of Fig. 2 of Paper 10 (ZnS.Cu) agree well with the Destriau formula, but those for ZnS.Mn deviate from a straight line by more than the experimental error.

I have derived an approximate formula for the brightness waves.† If n is the frequency, τ the lifetime of an electron in the conduction band, then the brightness increases with $\sin \delta$ where $\tan \delta = 2\pi n\tau$. Thus high frequency harmonics are favoured.

* See references (3) and (4) in discussion of Paper 7.

† CURIE, D. *J. Phys. Radium*, **14**, p. 674 (1953).

Paper 11

The physical chemistry of sulphide phosphors

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In order to make possible a description of the formation of phosphors by the concepts of physical chemistry, simplification of the chemical composition of the system and the conditions of preparation is indispensable. For a particular case, namely, ZnS, it is shown how preparation under controlled conditions may lead to a knowledge of the microstructure of the solid, and thence to an insight into the nature of the centres of luminescence and traps. It is shown that this knowledge is a necessary condition for the complete physico-chemical description of the formation of the phosphor in equilibrium with an atmosphere or a melt.

1. INTRODUCTION

The discussion of the preparation of phosphors in terms of the concepts of physical chemistry is only possible when the preparation is carried out under such conditions that equilibrium is reached. Further, for practical reasons, the system should be kept as simple as possible. Considerable simplification is achieved by omitting the flux, its functions being taken over by the combination of a high working temperature (causing recrystallization in the absence of a melt) and the addition of particular foreign ions (which would otherwise be donated by the flux). In this way both the number of different types of ions and the number of phases present is reduced.

As an example the preparation of ZnS phosphors in equilibrium with various atmospheres will be discussed. In the last section the equilibrium between solid phosphor and flux will be considered.

2. ZINC SULPHIDE WITHOUT FOREIGN IONS

If pure, oxygen-free ZnS powder is heated for a considerable time in H_2S at a temperature where the ZnS recrystallizes, e.g. 1100–1200° C, the product is practically non-luminescent at room temperature, but shows an ultra-violet band close to the fundamental absorption edge, the so-called "edge emission" at low temperatures.[1,2,3] This band has long been considered as being the fundamental fluorescence of pure, stoichiometric ZnS. Recent experiments on CdS, where a similar band appears,[4] indicate that this is probably not the case, and it has been suggested that the band is due to interstitial atoms. Yet, as we shall see, reduction, which might lead to interstitial zinc atoms, causes centres for a different band (green) and the intensity of the edge emission decreases. Therefore the ultra-violet band cannot be due to interstitial zinc. On the other hand, experiments on ZnO[5] show that although the intensity of the edge band is very low in reduced samples, the centres responsible for it are still there in appreciable concentration. Therefore the band cannot be due to interstitial sulphur either (or cation vacancies). The available data seem to be in best agreement with the assumption of a comparatively large concentration of centres independent of the atmosphere used in preparation and accordingly independent of deviations from exact stoichiometric composi-

tion. The original model, in which the edge emission was attributed to transitions between the lattice bands or to excitons, was, of course, in agreement with this requirement. If this model has to be rejected on the basis of the experiments on CdS,[4] then a solution might be found in the direction of dislocations or twinning sites connected with alternating structures that have been observed.[6,7,8]

If ZnS is heated under reducing conditions (i.e. in an atmosphere of hydrogen or zinc vapour) a phosphor results which shows a green luminescence and phosphorescence instead of the edge emission. Evidently this green luminescence is related to the presence of an excess of zinc above the exact stoichiometric composition.[9,10] This excess of zinc must be present either in the interlattice, or at normal lattice sites giving rise to sulphur vacancies.

As far as optical and electrical properties are concerned, sulphur vacancies and interstitial zinc atoms must be expected to behave similarly, and therefore the question which of the two mechanisms of incorporation is actually realized cannot be answered by studying these properties. It will be assumed below that an excess of zinc gives rise to the formation of sulphur vacancies; it must be emphasized, however, that all the following arguments involving these vacancies apply equally well to interstitial zinc atoms.

Starting with the assumption of anion vacancies it is probable that the centres responsible for the green luminescence are not simple anion vacancies, but anion vacancies that have attracted one electron (V_A^-).[11] Excitation corresponds to the liberation of an electron from this centre into the conduction band, fluorescence taking place upon recombination.

Thermoluminescence experiments reveal a simple glow spectrum, consisting of one peak at approximately 160° K corresponding to a trap depth of approximately 0·3 eV. It is likely that these traps are formed by the same centres: V_A^- has an effective charge $+|e|$ with respect to the surrounding lattice and, therefore, must be expected to be able to trap electrons in helium-like wave functions.

The situation in which the level V_A^- is occupied, but that of V_A^{2-} is empty is only realized when the system has been reduced weakly. Stronger reduction should result in a situation in which all the levels V_A^{2-} are occupied, the levels V_A^- no longer being there; accordingly, the intensity of luminescence should decrease with increase of the degree of reduction. Preliminary experiments indicate that this is actually the case.

Preparation of pure ZnS under high sulphur pressures, which might lead to the formation of cation vacancies, has so far not been attempted. There are some experiments,[12,13,14] however, which may be explained by assuming the presence of such vacancies in the lattice: heating at a high temperature resulted in the occurrence of a weak blue luminescence, the band usually referred to as the band of self-activated ZnS. Although the conditions of the experiments were far from ideal (no controlled atmosphere, and a base material which at least at the start contained chlorine), it will be tentatively assumed that the results are significant for pure ZnS, and are to be explained by the formation of zinc vacancies.[13,15] In accordance with this model, the formation of blue centres is not hindered by the addition of sulphur during the preparation.[55] In connexion with other properties of ZnS, in particular the effects of foreign ions to be discussed below, and with similar effects in CdS, it is possible to define this model more precisely by assuming that the centre responsible for the blue band is a cation vacancy that has lost one electron (V_C^+).[11] The level of a "normal" cation vacancy V_C is supposed to lie much higher, perhaps even in the conduction band, and does not play a part in explaining the luminescence properties of ZnS.

3. THE OXIDIZING OR REDUCING POWER OF THE ATMOSPHERE

In connexion with the above considerations it may be asked what factor determines whether a certain atmosphere acts as an oxidizing or as a reducing agent.[16] To answer this we may consider the case of a sample of exactly stoichiometric ZnS in a closed container. Then an atmosphere consisting of Zn and S_2 will be present, with

$$p_{Zn}p_{S_2}^{\frac{1}{2}} = \text{constant}$$

but in general

$$p_{Zn} \neq \tfrac{1}{2}p_{S_2}.$$

When extra gases are introduced, these may either leave the sulphur : zinc ratio in the atmosphere unaffected (neutral gases), or they may change this ratio by reacting with either of them. Gases which tend to decrease the sulphur pressure (and, accordingly, increase the zinc pressure) are reducing agents. On the other hand, gases which tend to increase the sulphur pressure are oxidizing agents.

Obviously zinc vapour and hydrogen are reducing agents, and the same is true of oxygen.[17,18] Sulphur is an oxidizing agent. Whether H_2S acts in one way or another depends on whether the sulphur pressure formed by the dissociation of H_2S is greater or less than the sulphur pressure above stoichiometric ZnS. The former is known, but the latter is not: therefore the character of H_2S has to be determined from the way it affects the optical and electrical properties of ZnS. In this manner it is found that at 1100° C H_2S is a weakly oxidizing agent, while at 1200° C it is nearly neutral.

Apart from the effects foreign gases may have on the composition of the atmosphere above the sample, such gases may also cause a variation in the way in which the solid responds to a given atmosphere. This may happen when foreign atoms from the gas enter the solid. At present, examples of this effect cannot be given. It is possible, however, that oxygen acts in this manner, a stoichiometric mixed crystal ZnS–ZnO requiring values of p_{Zn} and p_{S_2} that are different from those of pure ZnS.

4. CHARGE COMPENSATION: THE EFFECT OF FOREIGN MONOVALENT OR TRIVALENT IONS

The centres V_C^+ and V_A^- introduced above are charged effectively $-|e|$ and $+|e|$ with respect to the normal lattice. Since the crystal as a whole must be neutral, such centres can only be formed when this charge is compensated. In pure ZnS this may happen either by the formation of centres carrying opposite charges or by the incorporation of free charge carriers (electrons or holes). When foreign ions are incorporated in the lattice such ions may also take part in the compensation, provided their valency differs from that of the lattice ions they replace. In this manner many of the effects which foreign ions have on the properties of ZnS can be explained.

If V_C^+ is formed in pure ZnS, for instance, its effective negative charge should be compensated either by the simultaneous formation of V_A^- or of V_A. As a consequence the formation of V_C^+ is hindered not only by the possibly high energy of formation of these centres themselves, but also by that of the compensating vacancies. The formation of V_A^- or V_A becomes unnecessary, however, when foreign ions are introduced which represent an effective positive charge.

This is the case when S^{2-} ions are partly replaced by halide ions (Cl^-, Br^-, I^-),[19,3,20] or when Zn^{2+} ions are replaced by trivalent ions (Al^{3+}, Ga^{3+}, P^{3+}, As^{3+}).[21,15,23,24] If the energy of formation of a V_A^- or V_A centre markedly exceeds the energy involved in replacing a lattice ion by one of the foreign ions mentioned, then the introduction of foreign ions may lead to a concentration of V_C^+ centres that is considerably greater than that attainable in pure ZnS, and this is what has been found to occur.

Attempts to increase the concentration of V_A^- centres in a similar way by adding monovalent foreign cations (Ag^+) have so far failed.

Charge compensation by foreign ions not only increases the concentration of V_C^+ centres, but by the possibility of formation of V_C^+ centres the incorporation of foreign ions is stimulated at the same time. This function of the vacancy may in turn be taken over by centres of equal effective charge, such as are formed by replacing the divalent cations of the lattice by monovalent cations like Ag^+, Cu^+, Au^+,[3,20,21] Na^+, Li^+,[22] and probably also Pb^+.[10] Thus we arrive at solid solutions of the type ZnS–AgCl, Zn_2S_2–$CuAlS_2$, etc.

Apart from the solubility effect the function of the monovalent quasi-ion V_C^+ as a fluorescence centre is also taken over by the foreign monovalent cations, all of them causing occupied local levels above the valency band which may play a role in luminescent transitions.

In principle the foreign ions of opposite polarity attract each other and there is a tendency to form pairs. Yet these pairs may dissociate at the relatively high temperature of preparation and this situation may be frozen in when cooling to room temperature takes place. From the fact that the position of a level caused by a particular ion is independent of the type of compensating ion, it may be concluded that these ions do not belong to the centre, i.e. the centre is a foreign ion far from its compensating ion.

In comparing the luminescence bands caused by the various monovalent cations, it is seen that although there are differences between them, these are much smaller than should be expected if the levels involved were characteristic of the foreign ions. This leads to the assumption that the charge, rather than the character of the foreign ions, is important and that the levels playing a part in the luminescence are levels of the surroundings of the foreign ions, perturbed by their effective negative charge.

To a first approximation it can be said that electrons bound in the local levels belong to the sulphur neighbours of the foreign cations.[25,26] In such a case we may speak of indirect activation.[27] This assumption finds support in the fact that the position of the centre levels with respect to the valency band varies only slightly with incorporation of CdS,[26,28] and in the occurrence of new bands with incorporation of ZnO or ZnSe.[18,25]

Similar reasoning holds for the monovalent anions or trivalent cations which represent an effective positive charge: such ions cause unoccupied local levels close to the conduction band which may act as electron traps.[29] In this case also the position of the levels is independent of the compensating ions and varies comparatively little with the character of the ions themselves.

The small variation between the position of levels caused by different ions (and this applies to the occupied "activator" levels as well as to the traps) indicates that the activation is not entirely "indirect"; apparently electrons in these levels still spend part of their time in the electronic cloud of the foreign ions.

Apart from the levels caused by perturbation some of the foreign ions also produce levels which are characteristic of these ions, systems containing such ions showing characteristic absorption and luminescence bands in addition to the bands discussed above. This has been observed with the trivalent cations Pr^{3+} and Ce^{3+}. In these cases differences between the characteristic spectra for systems containing different compensating ions (e.g. Pr^{3+}, Ag^+ *versus* Pr^{3+}, Cu^+) indicate a certain degree of pair formation between the compensating ions.[21,30,36]

Since the radii of the foreign ions are in general different from those of the lattice ions which they replace, incorporation of foreign ions must cause a contraction or expansion of the lattice. Thereby the lattice energy is changed and, accordingly, the position of lattice levels is altered. The variation is extremely small, however, when the concentration of foreign ions is low, and this is invariably the case. As will be shown in Section 6 this effect is important for divalent ions, which may be incorporated up to much higher concentrations.

5. ZINC SULPHIDE CONTAINING COPPER

Copper as an activator needs special consideration since it gives rise to a blue, green, orange, or red luminescence dependent on the conditions of preparation. In the presence of compensating ions (Cl, Al) a green band appears when the copper concentration is smaller than the concentration of compensation ions, and a blue band when the copper concentration exceeds the concentration of compensating ions by a factor of about two, provided the preparation has been carried out under sufficiently reducing conditions, and that the copper concentration is $\geqslant 10^{-4}$ g. atoms per mole ZnS. These facts can be explained by assuming that both centres have an effective charge $-|e|$, while the green centres contain one, and the blue two copper atoms. The green centres are then Cu^+ at a lattice site and the blue are pairs of Cu^+ at a lattice site with Cu° at an interlattice site nearby ($Cu^+Cu_{is}^\circ$).[31,21] Different explanations have been proposed,[12,32,32a] but these are not in agreement with all the experimental facts.[33] At higher concentrations (up to 6.10^{-3} atoms Cu per g. mole ZnS), for [Cu] $\gg$ [Al] a yellow and an orange band appear in addition to the green band. These effects are due in part to self-absorption in the copper centres, as also observed with ZnS–Ag, Al at high Ag concentrations,[21] and in part to association of Cu^+ ions with the compensating ions.[36]

The red centres are formed when copper is incorporated without compensating ions.[31,34,35,36] Under these conditions copper is incorporated either as CuS, or as Cu_2S, with the occupation of interstitial sites by part of the copper ions or the formation of sulphur vacancies. The centres then may be either Cu^{2+} ions at lattice sites or some complex such as $Cu^+Cu_{is}^+$, $Cu^+V_A^-$ or $(Cu^+)_2V_A$.

6. EFFECTS OF DIVALENT FOREIGN ANIONS AND CATIONS

Divalent foreign ions can replace the divalent ions of the base lattice without the complications arising from charge compensation. In general two effects are to be expected upon incorporation of such ions, namely the occurrence of levels characteristic of the foreign ions, and an influence on the position of lattice levels by a change of the Madelung energy due to contraction or expansion of the lattice.

CdS and ZnS form an uninterrupted series of solid solutions. A gradual shift of the fundamental absorption from the position it has in pure ZnS to that in CdS must be explained by a mixture of the two effects mentioned above; separate

levels due to cadmium ions are not observed, probably because the wave functions of Cd^+ and Zn^+ overlap to a large extent.[1,2] If the position of local levels is also taken into account it is found that, apart from a few exceptions, the effect of cadmium can be described by a lowering of the conduction band, the position of all other levels remaining practically unchanged.[37-42,29] Such an effect is to be expected for the activator levels of the "indirect" type which stand in a generative relation to the valency band. The trapping levels are derived from the conduction band, and should remain at a fixed distance from this band, which is not the case. This point needs further consideration.

Magnesium sulphide dissolves in ZnS up to 20 mol %; within this range a shift of the fundamental absorption of ZnS to shorter wavelengths is explained by contraction of the lattice.[43] Levels of Mg^{2+} itself are not observed because these lie outside the forbidden energy gap.

Divalent cations giving rise to characteristic local levels are the ions of the transition metals Mn, Fe, Co and Ni. Of these, only the former two have been found to cause luminescence. For manganese it has been established that the luminescence is characteristic of Mn^{2+}, taking place between excited levels and the ground level of these ions.[1,2] For iron the same is probably the case.[44] Ni^{2+} and Co^{2+} equally give rise to characteristic ground levels and excited levels, and transitions between these have been observed in absorption.[25] Luminescence does not occur, probably because of non-radiative transitions. In addition, these ions give rise to empty levels which may act as electron traps.[45] By trapping an electron the ions are transformed into monovalent ions Co^+ and Ni^+.[29] This trapping action, combined with the large probability for non-radiative transitions within or near to the divalent ions (which are reformed when the trapped electron recombines with a hole), explains the "killer" activity of these ions.[46-49, 25, 56]

In solid solutions of ZnS–ZnSe selenium has the two effects one would expect: it causes (Se^{2-}) levels above the full (S^{2-}) band, and in addition causes a shift of the fundamental band due to expansion, as was found for ZnS–CdS. When monovalent cations A^+ are present, indirect activation leads to $Se^{2-}(A^+)$ levels in addition to the normal $S^{2-}(A^+)$ levels. Therefore with increasing ratio of Se : S the emission spectrum is not simply shifted, but it shows a shift and a transition from one band [due to $S^{2-}(A^+)$ levels] to another band [due to $Se^{2-}(A^+)$ levels] at the same time.[25]

In discussing the effects of oxygen on ZnS a distinction must be made between the purely physical effects of oxygen replacing sulphur (in a solid solution ZnS–ZnO) and the reducing effects of oxygen or oxides on sulphides (see Section 3), which in turn has physical consequences (see Section 2). It seems that both effects are present:[18] O^{2-} incorporated in ZnS behaves like Se^{2-}, causing levels above the valency band as well as indirect-activation levels $O^{2-}(A^+)$. A glow spectrum observed with phosphors containing oxygen was also originally attributed to O^{2-}. Comparison of the three glow peaks observed (corresponding to trap depths of approximately 0·2, 0·3 and 0·6 eV) with the glow peak found in reduced ZnS (0·3 eV, see Section 2) shows, however, that the middle peak is probably due to reduction. The remaining peaks may still be due to O^{2-}.

7. PHYSICO-CHEMICAL EQUILIBRIA WITHIN THE SOLID AND BETWEEN A SOLID AND THE ATMOSPHERE

Attempts to change the properties of ZnS phosphors by physico-chemical methods and thus to derive the fundamental constants such as reaction constants and energies of formation of particular centres have been very few. This has been done for the formation of self-activation centres and traps, but owing to the uncertainty of the reactions involved the exact meaning of the results is still uncertain.[13,14] A physico-chemical description of the formation of centres in ZnS . Cu(Cl) phosphors in equilibrium with atmospheres of $H_2 + H_2S + HCl$ has been given.[50] This work emphasizes the importance of quantitative knowledge about the gas atmosphere (chlorine pressure, oxidizing or reducing power) in connexion with the final composition of the phosphor, and discusses the effects internal equilibria may have (association and dissociation of incorporated compounds or complexes). Yet it is still subject to criticism. In the first place the model used for the centres in self-activated ZnS (= Zn^+) is no longer accepted; replacement of Zn^+ by the modern centre model (V_C^+) leads to slightly different equations, though owing to the comparatively weak influence of the reducing power of the atmosphere, the agreement with experimental data remains practically the same. More serious is the fact that the formation of vacancies has been neglected while the influence internal electronic equilibria may have on the chemical equilibria has not been taken into account. The consequences of these omissions cannot be estimated before the magnitude of the constants regulating the formation of lattice imperfections, and the position of energy levels caused both by these imperfections and by foreign ions, are known. This is not yet the case.

A complete treatment, involving all these factors, of the equilibrium between a solid and the atmosphere has been given recently for CdS.[51] A similar treatment for the equilibrium solid-melt (though neglecting vacancies) has been given for Ge.[52]

8. EQUILIBRIUM SOLID PHOSPHOR—MOLTEN FLUX

Equilibria between a solid phosphor and a molten flux can be described in two ways leading to the same result. In one description chemical reactions that may occur between the phosphor and the flux are discussed, while reaction products that are formed are thought to be distributed in a certain proportion between the two phases.[53] The second type of description starts from the situation initially present, in which the pure solid phosphor and the pure flux are present in contact, and considers the equilibrium which results when *all* kinds of ions present distribute themselves between the two phases. In the system $(ZnS)_S - NaCl_L$, for instance, both Zn and S dissolve to a certain extent in the NaCl, and on the other hand, both Na and Cl enter the ZnS. It has been found that ZnS heated with NaCl contains both chlorine and sodium,[22] while ZnS made with a $MgCl_2$ flux contains chlorine and magnesium.[43, 53] The concentration in which the various ions enter the other phase need not be equal, provided electroneutrality is maintained in some way or other.

When activators are present these participate also in the distribution equilibrium as has been demonstrated for SrS . Eu, Sm and SrS . Ce, Sm phosphors prepared with $SrCl_2$ as a flux.[54] Even for a melt, charge compensation seems to be easier if it takes place by means of foreign ions than by formation of vacancies: when oxygen is present the distribution of Sm^{3+} between the phosphor and the flux is shifted in the direction of the latter, which can be explained by assuming that the simultaneous replacement of Sr^{2+} by Sm^{3+} and Cl^- by O^{2-} leads to the formation of SmOCl which fits easily into the $SrCl_2$ "structure" of the melt. A similar reasoning holds for Ce^{3+}. Solution of Eu^{2+} does

not involve such a process and for this ion the distribution coefficient has indeed been found to be unaffected by oxygen.

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DISCUSSION

Mr. J. Ewles: If the efficiency of the edge emission of zinc sulphide (heated in H_2S for a long time) is appreciable the product cannot be described as non-luminescent. What is the evidence for interstitial cadmium in cadmium sulphide and why should interstitial zinc and sulphur vacancies behave similarly?

We have evidence that anion vacancies produce luminescence effects in alkali halides, silica, alumina and calcium oxide.[1,2] The suggestion that different foreign ions produce luminescence effects by perturbation of lattice states is very similar to that made by Ewles and Lee.[2]

Dr. S. Rothschild: Dr. Kröger has stated that zinc sulphide heated under strong reducing conditions gives a phosphor with green fluorescence and phosphorescence due to excess of zinc. Similar results were obtained when zinc sulphide phosphors were prepared by the violent reaction of zinc, sulphur and 5% sodium chloride.[3] The phosphor showed a green fluorescence and afterglow, although no copper could be detected in the starting materials. The green luminescence could not be removed by washing with acetic acid and was therefore not due to zinc oxide, but probably to excess zinc. It would be interesting to investigate whether cadmium sulphide heated under reducing conditions shows a band in the red or infra-red, and the energy distribution shown by ZnS.CdS phosphors produced under the same conditions.

Kröger's theory of "self-activated" zinc sulphide may explain why no discontinuity has been observed in the shift

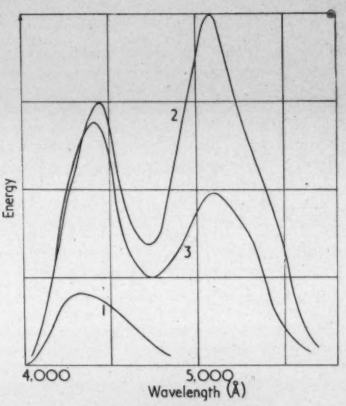
of the emission band of self-activated zinc sulphide phosphors when zinc is replaced by cadmium. According to previous assumptions the emission is caused by the presence of excess zinc. Leverenz[4] stated that the replacement of zinc by cadmium should cause the appearance of new bands as in the case of sulphur replaced by selenium in zinc sulphide. If the centre consists of a cation vacancy which has lost one electron this difficulty is removed and the colour shift is due to the change in the constituents of the surrounding lattice.

Kröger's theory of V_A^- centres also explains why it is possible to prepare CdS.Ag phosphors without addition of halides or other elements for charge compensation.[5] Halides are generally added to ZnS phosphors to assist in crystallization and not only for charge compensation, but CdS phosphors crystallize fairly well even without the addition of fluxes.

Dr. N. Arpiarian: There is experimental evidence which suggests that the "killer" centres due to iron or nickel in zinc sulphide are normally occupied, while those due to cobalt are normally empty. Thus the Fermi level appears to lie between the iron or nickel levels and those of cobalt. For nickel or iron the killer effect is more noticeable at longer decay times; but for cobalt, radiationless transitions occur immediately after excitation and the fluorescence is quenched.[6] Other evidence is from build-up of fluorescence and from absorption in the 3650 Å region.[7] It is suggested that the change in the Fermi distribution with decrease in temperature[8] accounts for the similar behaviour of Fe, Ni and Co at low temperatures in ZnS, the Co centres being normally occupied at low temperatures.

Dr. W. Hoogenstraaten: Dr. Arpiarian suggests that in ZnS.Cu the level caused by Co is empty in the unexcited state, but occupied in the case of Ni. This is in contradiction with experiments in which we have shown that the introduction of Ni into ZnS.Cu gives rise to traps. Because of the great depth of the traps and the temperature quenching of the phosphor, these traps cannot be shown by the glow curve experiment, but only indirectly by the slow build-up of fluorescence when the traps have been previously emptied by infra-red irradiation. The build-up becomes slower as more nickel is present in the phosphor.[9] The different effect of Co and Ni on the phosphorescence of the copper emission is easily explained by the difference in trap depth of the Co and Ni levels, the Co trap depth being less than the activation energy necessary for hole transfer from the Cu levels, while the Ni trap depth is greater than the activation energy.

Dr. E. Grillot: To explain the green and blue emission bands in ZnS.Cu phosphors I have suggested that blue emission is due to a copper ion surrounded by sulphur ions only and that green emission is due to the substitution of an oxygen ion for a sulphur ion in the surroundings.[10] In addition to previous support for this view,[11] there are the following facts.[12] Heating ZnS with 1% NaCl at 1200° C followed by prolonged washing of the sample gives $3{\cdot}8 \times 10^{-5}$ g ion of Cl per mole in the specimen, which has a weak blue emission. Reheating at 500° C for 1 hour produces no change (see Curve 1 of the figure), but if $7{\cdot}5 \times 10^{-5}$ g ion of Cu per mole is added, heating at 500° C produces intense luminescence with two emission bands (Curve 2). The marked green afterglow proves that the corresponding centres are those of ZnS.Cu (10^{-4} to 10^{-5} g ion of Cu per mole, as shown by radiochemical analysis). Treatment of the ZnS.Cu with HCl removed the original surfaces with a marked change in spectral emission (Curve 3). It is not easy to see that a valency change could occur with the degree of copper penetration, and I suggest that near the surface the predominance of green emission is due to superficial oxidation.



Spectral emission of ZnS

Curve 1, heated with NaCl only.
Curve 2, reheated with Cu.
Curve 3, treated with HCl.

Dr. P. W. Ranby: The preparation of oxygen-free ZnS is a matter of speculation especially when the material is prepared by precipitation from aqueous solutions. Prolonged heating of the zinc sulphide in atmospheres such as H_2 and H_2S will remove large amounts of oxygen from the material, but it is open to criticism as a method for reducing the oxygen concentration below a value at which a corresponding concentration of, say, copper would still affect the luminescence. This is another example where ordinary chemical analysis is of little use, and a physical or radiochemical method may be necessary to establish whether the starting material is really oxygen-free.

Author's reply: It has been questioned whether the principle of charge compensation, which seems quite evident for ionic crystals, may be applied to crystals like ZnS which are largely covalent. The principle may be so applied since it is based, not on a particular distribution of charge, but on the fact that atoms tend to combine in specific proportions to form compounds. Addition of Ag_2S to ZnS must be accompanied by formation of S vacancies or interstitial metal atoms irrespective of the type of lattice. On the other hand, these complications are not needed when AgCl or $(Ag, Al)S_2$ is incorporated.

In reply to Mr. Ewles: (*a*) The efficiency of the edge emission of ZnS at low temperatures has not been measured. We know, however, that it has not reached its maximum at −180° C, and so the efficiency that may be reached is probably quite appreciable.

(*b*) Interstitial Zn^{2+} and sulphur vacancies have in common an effective charge of 2^+ with respect to the normal lattice. Therefore both may trap two electrons, one at a deep level, the second at a higher level. The exact position of their levels may differ, but this difference will probably not be very large.

(*c*) The concept of vacancies is certainly not restricted to ZnS: I agree that it probably may be held responsible for many of the effects observed with CaS and CaO phosphors.

In reply to Dr. Rothschild, I agree that the green luminescence observed by Coustal probably was not due to

copper, as he assumed, but to a stoichiometric excess of zinc.

In reply to Dr. Grillot, the model proposed for the blue copper centre is very simple and, therefore, very attractive. Yet it cannot be the correct one, because oxygen-free phosphors can be made showing a strong green copper band, e.g. (*a*) ZnS (precipitated from a zinc salt by thiosulphate) + 10^{-5} Cu, fired in 80% H_2S–20% HCl at 1200° C, fluoresces strongly green; (*b*) The same ZnS + 10^{-5} Cu + $CaCl_2$, fired at 1200° C in oxygen-free N_2, also shows a strong green luminescence. Only when NaCl is used as a flux is the luminescence blue without addition of oxygen and green with oxygen (see reference 18 of my paper). This effect must be specific for NaCl and may be explained by assuming that oxygen aids in liberating Cl^- from the sodium.

The green luminescence observed by Grillot at the surface of grains refired at 500° C with addition of copper is the "green II" previously discussed (reference 31 of my paper). Cooling to low temperatures causes the luminescence to become bright blue, which shows that the concentration of blue centres markedly exceeds that of the green centres. The absence of blue emission at room temperature is due to the killing action of the high concentration of copper in the surface layer.

In reply to Dr. Ranby, we have found that aluminium does not act as a co-activator if oxygen is present. Therefore the question whether ZnS is free of oxygen can be answered by studying the properties of phosphors containing aluminium. A ZnS phosphor with 10^{-4} Ag and 10^{-4} Al, and containing some oxygen, is very poorly luminescent when prepared in an atmosphere like nitrogen which leaves the oxygen in the sample. Prolonged heating in a sulphur-containing atmosphere like H_2S produces the strong blue luminescence characteristic of ZnS.Ag phosphors. Our explanation is that so long as oxygen is present, even in a concentration as low as that of the activator, aluminium remains as Al_2O_3 and does not dissolve in the ZnS. Heating in H_2S replaces the oxygen by sulphur and the Al_2S_3 so formed dissolves in the ZnS.

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Paper 12

Physical measurements and the nature of the luminescent centre

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Important information concerning the nature of the luminescent centre may be derived from comparatively simple physical measurements. Comparison of the temperature dependences of luminescence efficiency and decay rate gives information about the location of dissipative transitions and permits the calculation of activation energies and frequency factors for these transitions in certain cases. Information concerning the interaction of activators with their environment, as in sensitized luminescence and concentration quenching, is also derivable from these measurements. From additional measurements of the low temperature absorption and emission-band peaks and widths and the band-width variation with temperature, the configuration co-ordinate curve of a centre can be derived experimentally.

Information concerning energy transfer in non-photoconducting sensitized phosphors may be obtained from measurements of absorption (reflexion) spectra or of quantum efficiency as a function of composition. Similar measurements can demonstrate the formation of pairs or higher aggregates of activators and lead to a determination of oscillator strength.

There is as yet, unfortunately, no way of determining from first principles whether or not a given system will luminesce after it has absorbed energy. Configuration co-ordinate models discussed at the 1938 Faraday Society Discussion* offered general schematic representations of systems that divest themselves of absorbed energy either by luminescent transitions or by radiationless transitions, without indicating what types of physical system would follow each de-excitation scheme. While new luminescent systems discovered in the intervening years have, accordingly, been the result either of empirical research or of rather simple analogy, a large fraction of the experimental research effort has been directed at known luminescent systems in an attempt to learn more about their basic mechanisms. It is the purpose of this paper to survey some of the physical measurements that have been performed for this purpose, and to discuss their implications concerning the nature of the luminescent centre. It is realized that the types of physical measurements that can be made on phosphor systems is legion, when one considers all the optical, electrical, magnetic, and structural properties that are of interest.

* See *Trans Faraday Soc.*, 35 (1939).

Attention will be restricted in this paper to those comparatively simple measurements that are readily performed in the course of normal studies on phosphors, and which have a bearing on concepts of general importance.

Whether or not a given system will luminesce after absorption of energy is determined, of course, by the relative probability of a luminescent transition compared to the probabilities of a number of other processes that can dissipate the absorbed energy. Any information that can be obtained concerning these alternate mechanisms of de-excitation of an excited centre is thus of utmost importance. A direct experimental approach to such information was described by Kröger, Hoogenstraaten, Bottema, and Botden,[1] who applied to the temperature quenching of solid inorganic phosphors general considerations that have proved valuable in the study of temperature quenching, concentration quenching, and foreign-ion quenching of organic fluorescent systems.[2,3,4] The physical measurements involved in this technique are the determinations of both the quantum efficiency and the decay constant of a phosphor as a function of temperature.

As is well known, the quantum efficiency of phosphors remains essentially constant over a considerable range of temperature up to a certain point (the "thermal breakpoint") beyond which the efficiency decreases quite rapidly as the temperature is increased. This efficiency decrease is due to the increased probability of a radiationless transition at the higher temperatures. The shape of the efficiency *versus* temperature curve is satisfactorily accounted for by the expression[1]

$$\eta = A[1 + (b/a)]^{-1} \qquad (1)$$

where η is the quantum efficiency, a is the essentially temperature-independent probability of a fluorescent transition (defined as the reciprocal of the lifetime of the excited state), b is the strongly temperature-dependent probability of a radiationless transition, and A is the fraction of absorbed energy directly absorbed by the centre or transmitted to it. Considering, as the simplest case, a centre which is excited but not ionized by the absorbed radiation, the law describing the fluorescence decay at the lower temperatures, where the probability of the radiationless transition is negligible, is the well-known exponential decay law

$$I = I_0 e^{-at} \qquad (2)$$

where I_0 is the intensity of fluorescence at the instant of cessation of excitation, I is the intensity of fluorescence at a time t thereafter, and a has been defined above. If, now, above the thermal breakpoint, each excited centre has become susceptible to a radiationless transition with the probability b, the law describing the fluorescence decay is still exponential, but is given by

$$I = I_0 e^{-(a+b)t} \qquad (3)$$

where all the symbols have been defined above. Since a is independent of temperature while b is strongly temperature-dependent, the measured decay constant $c = (a + b)$ should not vary with temperatures at low temperatures where $a \gg b$, and should increase rapidly with temperature above the temperature at which b becomes appreciable with respect to a. In the simple case under discussion, then, the breakpoint of the decay constant *versus* temperature curve should coincide with that of the efficiency *versus* temperature curve. Using equations (1) and (3) the values of a and b can be calculated from the experimental data, A being considered a constant which causes an overall decrease in efficiency but which does not affect the shape of the efficiency curve. From the variation of b with temperature, derived in this way from experiment, the activation energy for the dissipative process can be calculated using the relation:[5]

$$b = b_0 e^{-\Delta E/kt} \qquad (4)$$

where ΔE is the activation energy and b_0 is a constant which should be of the order of the frequency of lattice vibrations. The activation energy ΔE is an important parameter in the experimental derivation of configuration co-ordinate curves and appears to be a characteristic of a luminescent centre which is very sensitive to environmental changes. Kröger and his colleagues have applied the foregoing method to the determination of ΔE for a number of luminescent systems.[1,6,7]

It has been assumed in the above discussion that only one excited state of the centre is involved, and that both the fluorescent and dissipative transitions start from this single excited state. In more complicated cases, two (or even more) excited states may be involved in the transition, the absorbed energy first raising the centre to a state higher than that from which the fluorescent transition occurs. A (non-radiative) transition from the higher state to the emitting state must then precede the actual emission process. Under these circumstances a dissipative transition can take place either from the emitting state or from the higher excited state reached initially. For certain specific models of centres of this type Kröger and Hoogenstraaten[6] were able to show rigorously that the decay constant is affected by the dissipative transition only if the dissipative process starts from the excited state of longest lifetime, i.e. from that excited state which determines the decay rate in the absence of the dissipative transition. When this is the case, a rapid increase of the measured decay constant accompanies the rapid decrease of luminescence efficiency with change in temperature. If the dissipative transition does not start from the excited state of longest lifetime, the decrease in efficiency with temperature is not accompanied by a corresponding increase in decay constant. It is reasonable to assume that this conclusion is true for all centres in which the emissive state is reached after transitions from higher excited states, even though a general proof of this proposition has not been given. The same type of measurements which has been found useful in obtaining quantitative values of the dissipative constants of a centre, is thus seen to be useful also for the qualitative purpose of locating the state from which dissipative transitions occur. Thus Kröger and Hoogenstraaten[6] were able to show that two dissipative processes occur in manganese-activated zinc silicate phosphors under 2537 Å excitation, one process starting from a high excited state, the other starting from the emitting state of the manganese. The first dissipative process is increased by iron impurity or by mechanical deformation of the phosphor, while these do not influence the second process. The location of the dissipative transitions thus facilitates the study of the interactions of the activator centre with its environment, and is an index of the effect of lattice defects, impurities, and also of identical activator atoms on the centre.

The interaction of an activator with atoms of the same species leads to the phenomenon of concentration quenching. As a further illustration of the usefulness of the physical measurements described above, their implications concerning this phenomenon may be mentioned. Many attempts have been made to explain the concentration-dependence of the efficiency of phosphors, the most recent being by Johnson and Williams[8] and by Ewles and Lee.[9] In both the pro-

posed models the drop in efficiency with increasing activator concentration is ascribed to a decrease in the effective number of emitting centres. In the formulation used by Johnson and Williams, for example, such a decrease in the effective number of emitting centres comes from the assumption that an activator can absorb but not emit if there is another activator ion situated on any one of the z nearest available sites, where z varies from phosphor to phosphor, and varies with temperature for a given phosphor. Since the fraction of activators situated within z sites of another activator evidently must increase with the activator concentration, a diminution of efficiency must ultimately occur at high activator concentrations. If these formulations were correct, the characteristics of activators that remain "isolated" (i.e. with no other activator ion in any of the z effective quenching sites) should not be affected. The dissipative constants of the "isolated" centres capable of emission should be independent of the total activator concentration. The breakpoint in the decay constant *versus* temperature curve should thus be independent of the activator concentration. Experiment shows, however, that this is not the case in typical phosphor systems. The breakpoint of this curve moves to lower temperatures as the activator concentration increases.[10,11] The mechanism of concentration quenching in these systems must therefore be one which makes available a dissipative process to all the activator atoms, rather than one which merely affects a certain fraction of them.

As a final illustration of the usefulness of the above-described measurements in exploring the nature of the luminescent centre, the application of this technique to impurity-sensitized phosphors may be mentioned. In such phosphors radiant energy is absorbed by one foreign atom, the sensitizer, and emitted by a second foreign atom, the activator.[12] Different impurities may function equally efficiently as sensitizers for a given activator in a given host crystal, and the luminescence spectrum of the activator is generally the same regardless of the nature of the sensitizer. Although no special interaction between the sensitizer and the activator is thus apparent from the emission spectrum, such an interaction can be detected from the different efficiency *versus* temperature curves obtained with different sensitizers, and confirmed by corresponding differences in the decay constant *versus* temperature curves.[7] An even more convincing demonstration of this interaction might be obtained by the same experimental measurements on a single sensitized phosphor, using first radiations absorbed only by the sensitizer and then radiations absorbed only by the activator. This would distinguish, by means of the experimentally determined values of b_0 and ΔE, between those activator atoms that interact with the sensitizer and those which do not. Since the activators in all impurity sensitized systems studied so far are ones that have forbidden transitions, the absorption in the activator itself would be feeble, and the experiment might be difficult to perform. In this event one might turn to sensitized systems of the dipole-dipole type predicted by Dexter.[13]

The field of sensitized luminescence offers further illustrations of the information that can be derived from comparatively simple physical measurements. A question that immediately arises in sensitized systems concerns the range of interaction between the sensitizer and the activator, i.e. how close must the activator and sensitizer be for energy transfer to occur with high probability? The possibilities that have been considered are (1) that the activator must occupy one of the equivalent nearest neighbour sites to the sensitizer,[14] and (2) that the number of such sites over which energy transfer is possible may be much larger than the few nearest neighbour positions.[14,15] In the latter case it becomes of interest to determine this number. The high activator quantum efficiencies measured in systems of known activator and sensitizer concentrations can be explained on the basis of the first postulate only if a non-random distribution of the two species is assumed.[14] No experimental evidence exists to support the assumption of a non-random impurity distribution in sensitized systems,[16] hence the sensitizer must be effective over many more sites than the nearest neighbour sites. When the interaction of the sensitizer and the activator affects the absorption or emission spectra of either one, means are at hand to count the fraction of each kind of atom that is involved in the interaction. As already mentioned, little or no change in activator emission spectrum is observed experimentally. This fact, combined with the feeble absorption of the activators usually of interest in sensitized systems, means that information on this point is not readily obtainable from such studies of the activator. In most cases the absorption and emission spectra of the sensitizer are likewise unaffected by its interaction with the activator. A system where such an effect appears to occur, however, is the $CaSiO_3$. Pb, Mn system, although here the situation is complicated by the occurrence of phase changes in the host crystal. Schulman, Ginther, and Klick,[15] have measured the progressive decrease in the characteristic Pb^{2+} absorption band upon the introduction of Mn^{2+} in this phosphor, as well as the corresponding growth of a new absorption band. On the assumption that these changes in the Pb^{2+} absorption are due to the interaction that permits energy transfer from Pb^{2+} to Mn^{2+}, it is possible to calculate the number of cation sites surrounding a Pb^{2+}, which, if occupied by a Mn^{2+}, will result in energy transfer. The number of sites found to be within the sensitizing range of the Pb^{2+} was thus found to be about thirty. This experimentally determined number agrees with a theoretical estimate by Dexter[13] of the sensitizing range to be expected for energy transfer by a dipole-quadrupole mechanism or by exchange effects.

Measurements of the quantum efficiencies of sensitizer and activator fluorescence as a function of sensitizer concentration have led Botden[16] to conclude that energy transfer from sensitizer to sensitizer also plays an important part in this type of luminescence. This conclusion would explain the dependence of transfer efficiency on sensitizer concentration that Botden observed. From the dependence of the ratio (activator efficiency)/(total luminescence efficiency) *versus* sensitizer concentration, and from the first and second derivatives of this curve, he was able to compute the ranges both of sensitizer-activator transfer and sensitizer-sensitizer transfer. For manganese-activated phosphors the former value was of the order of thirty cation sites surrounding the sensitizer, as found by the previous workers. Sensitizer-sensitizer transfer was found to occur over longer distances; for cerium this range was found to be about 150 cation sites. Ginther,[17] however, was able to show that the dependence of transfer efficiency on sensitizer concentration in another cerium-sensitized phosphor, CaF_2 . Ce, Mn, is due to the formation of Ce^{3+}–Ce^{3+} pairs or aggregates with a different sensitizing range than that of isolated Ce^{3+} singlets. These aggregates exist in considerable numbers at the high cerium concentrations normally used in Ce^{3+}-activated or Ce^{3+}-sensitized phosphors, and make their presence evident by introducing new absorption and excitation bands not found at low cerium concentrations. Thus, sensitizer-sensitizer transfer, although an *a priori* possible auxiliary mechanism

for energy transfer, need not occur in all cases. Indeed, to prove that it plays a role at all, it is necessary to ensure by appropriate measurements that pairs or other sensitizer aggregates do not act as sensitizing centres with their own characteristic sensitizing range.

In this connexion it may be mentioned that the formation of pairs or higher activator clusters or complexes has been invoked to explain a variety of luminescent effects. In favourable cases it is possible to demonstrate the existence of these activator groups in an approximately quantitative fashion by appropriate physical measurements. Such a case, for example, is the formation of Ag^+–Ag^+ pairs in NaCl . Ag.[18] Qualitative indications of pair formation are (*a*) the growth, with increasing silver concentration, of a new absorption band to the long wavelength side of the characteristic Ag^+ bands and (*b*) the different emission band obtained by irradiation into the new band. Assuming a random distribution of activators in the host crystal, and knowing the structure of the crystal, one can readily calculate from probability considerations what fraction of activator atoms are isolated from atoms of the same kind, and what fraction of the activators have another activator atom on one of the equivalent nearest-neighbour sites, etc., that is, the fraction of singlets, pairs, triplets, and higher aggregates as a function of the total activator concentration. The rates of change of the numbers of singlets, pairs, etc., with concentration are different. A comparison of the experimental plot of absorption coefficient *versus* activator concentration with the calculated distribution of the various species as a function of activator concentration thus identifies the number of activator atoms in the centre corresponding to the absorption band under consideration. To construct the experimental curve one should, strictly speaking, plot the quantity $n_0 f$ *versus* activator concentration, rather than the absorption constant at the peak of the band; n_0 is the concentration of absorbing centres per cubic centimetre, and f is the oscillator strength. The product $n_0 f$ is obtained from the measured spectral absorption curves by means of Smakula's equation.[19,20] From the known activator concentration and the foregoing assignment of bands to singlets, pairs, etc., the actual concentration of each species of centre can be determined, and the corresponding values of the oscillator strength can be calculated, which gives a measure of the degree of "forbiddenness" of the absorption transition. In the case of NaCl . Ag cited above, single crystals were available, which facilitated the making of absolute absorption measurements. In most phosphor work such crystals cannot be prepared and one is constrained to work with powders. In these cases resort may be had to measurements of reflexion spectra instead of absorption spectra, with computation of the absorption spectra from these data by the method of Johnson.[21]

The information that can be derived from measurements of the temperature dependence of the quantum efficiency and of the decay constant has been described above. The temperature dependences of emission and absorption band widths are two other experimental quantities that yield considerable insight into the nature of the luminescent centre. Use has frequently been made of low temperatures, of course, to resolve emission bands that overlap at normal temperatures, taking advantage of the fact that the band width varies approximately as $T^{1/2}$ corresponding closely to classical theory. Departures from this behaviour become greater as the temperature decreases, however, the bands being considerably broader at low temperatures than this relation predicts.[22] Even at liquid helium temperature, for example, the band width of typical phosphors amounts to several hundred ångströms. Such a large spread in emission frequencies at this low temperature, even with phosphors that have very low activator contents, has been explained on the basis of zero-point vibrations of the luminescent centre.[22,23]

Klick[24,25] has shown how the configuration co-ordinates of a centre can be found experimentally from the peak frequencies and widths of the absorption and emission bands at low temperature and the temperature dependence of the band widths. Additional necessary data may be obtained from the temperature dependence of the efficiency and decay constant, which, as described earlier, yield the value of ΔE, the energy separation between the lowest level of the excited state and the point in the configuration co-ordinate diagram where the excited state and ground state curves "intersect." The results obtained by this experimental method of configurational co-ordinate determination agree reasonably well with those obtained by computations from theory.[26]

Applying this method to manganese-activated zinc silicate, Klick and Schulman[27] showed that the skewed spectral energy distribution of the emission of this phosphor can arise from the small separation of the minima of the excited state and ground state curves in the configuration co-ordinate diagram, and that it is not necessary to assume this spectrum to be due to the superposition of a number of Gaussian subbands. This conclusion is in accord with the negative results of experiments designed to detect the existence of these subbands, such as the measurement of excitation spectra,[28] low temperature emission spectra,[29] and emission spectra as a function of decay time.[29,30]

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DISCUSSION

Dr. F. E. Williams: The calculation of transition probability for emission, emphasized by Dr. Schulman, is of secondary importance to the theory of the luminescence of thallium-activated potassium chloride. The electronic transition involved ($^3P_1^0 \rightarrow {}^1S_0$) occurs in the free thallous ion with an appreciable transition probability, and the effect of lattice perturbation is to enhance this probability.

As regards the dependence of luminescence efficiency on activator concentration, the theory of Johnson and Williams (reference 8), in the general treatment, accounts for the dependence on activator concentration of the efficiency *versus* temperature function. The activation energy ϵ_z for the activator system with no other activator ions among the z nearest neighbour sites, but with an activator at the $(z + 1)$ site, is deduced from the activation energy ϵ_0 for infinite dilution. In the cases in which the reduction is due to an interaction such as exchange which depends on the extension of the wave functions, ϵ_z is a function of the distance r to the $(z + 1)$ site: $\epsilon_z = \epsilon_0[1 - \exp(-ar)]$, where a is a constant. The efficiency of the phosphor is

$$\eta = \sum_z f_z[1 + (s/A)\exp(-\epsilon_z/kT)]^{-1}$$

where f_z is the fraction of the activators characterized by z.

Dr. H. A. Klasens: The effect of the Mn concentration in magnesium arsenate on the temperature dependence of this phosphor confirms that there is an interaction at long distances before total quenching occurs. When the activator content is increased the temperature dependence curve is shifted to lower temperatures. The change of the activation energy E with average distance r between the activators can be represented fairly accurately by the relation given by Johnson and Williams (Paper 12, reference 8) with $\epsilon_0 = 1{\cdot}45$ eV and $a = 0{\cdot}075\,\text{Å}^{-1}$.

Dr. E. Nagy: We have studied the quenching effects of "killer" impurities and temperature in some phosphors.(1) To measure optical absorption coefficients with 10% accuracy we used diffuse reflexion from layers of uniform grain size, treating the results by the theoretical methods of Bodó. For zinc silicate containing manganese and traces of iron the absorption coefficient is given by the sum of those for the manganese and for the iron, each of these being linear with concentration over the range studied. The coefficient for 1% Mn is high ($600\,\text{cm}^{-1}$), and probably due to an allowed transition between matrix levels and the manganese. The linear dependence rules out the possibility that killer-activator pairs are formed. Another common trace impurity is titanium giving a coefficient as high as that for manganese. For long wavelength ultra-violet excitation the manganese emission is severely affected by iron, since the manganese absorption is low compared to that for 2537 Å radiation, whereas that for iron is almost unchanged. However, there is evidence of energy transfer from activator to killer centres.

Temperature dependence of emission with killers present is complex. A quenching process with activation energy 0·2–0·6 eV is associated with the dielectric loss effects while another with activation energy 1·6–2·6 eV is an inner quenching in the activator centres.

Pairing of activator and killer centres would be indicated by a pressure dependence of the quenching, but no such effect was observed for the above silicates or for halophosphates activated by manganese and antimony. An effect does occur for zinc sulphides.

Dr. J. H. Schulman: This paper was limited to physical measurements normally available in luminescence laboratories. It is well to call attention, however, to the information given by paramagnetic resonance absorption experiments, which promise to be of great use in the study of luminescence systems. Several authors(2,3,4) have thus obtained information about the valency of activators in phosphors, and about activator interactions with each other, with other impurities in the crystal, and with the crystal field.

Mr. J. Ewles: One of the difficulties of fundamental research is to obtain a perfectly non-luminescent starting material. The most important question is what determines the radiative transition probabilities. Efficiency is not usually constant over a wide range of temperature as in the law $\eta = A(1 + b/a)^{-1}$. Of ten CaO phosphors studied at Leeds only one obeyed this law even approximately. The temperature dependence of efficiency is too complicated to be explained by a simple radiationless process.

According to the theory of concentration quenching of Ewles and Lee,(5) and of Johnson and Williams,(6) the efficiency is determined by the quenching interaction of large centres with others of the same or of different kinds. Dr. Schulman seems to have overlooked the fact that the theory does indeed account for the initial increase of efficiency with concentration which always occurs. He further objects that the large centre should retain all its characteristics at all concentrations. I do not think that this can be maintained but when the most individual characteristic of a centre—the emission spectrum—can be studied in exact detail, as for Bi- and Pb-activated Ca and Sr oxides and sulphides, it is found that the resolved spectra are independent of concentration. Although Schulman accepts the idea of long-range action of sensitizers over many lattice sites he appears to reject the most obvious explanation, namely, large centres.

Dr. T. P. J. Botden: What is to be understood by "pairs," for instance the Ce–Ce pairs in $CaF_2.Ce$? The two Ce atoms are not necessarily situated on the adjacent cation sites. Only a strong interaction is needed between them, which may well exist over longer distances.

Author's reply: In reply to Dr. Williams, in my paper I refer to the absence of a theoretical treatment of the luminescent centre which can truly claim to start from first principles. The fact that luminescence does occur in KCl.Tl does not mean that a calculation of the radiative and non-radiative transition probabilities is of only secondary importance in the theory of the luminescent centre. It means rather that the questions considered in Williams' elegant work on KCl.Tl comprise only part of the fundamental problem, and leave unanswered the basic question, "Does the system luminesce with appreciable efficiency?" This point is illustrated by his examination of KCl.Mn. Here complete disagreement with experiment results from the assumption that only transitions which have an "appreciable" probability

in the free Mn^{+2} ion need be considered. Experiment in this case guides theory, and teaches us that transitions are involved which are forbidden in the free Mn^{+2} ion. The present inadequate state of theory with regard to the luminescence of the *F*-centre emphasizes this point, where theoretical predictions of the spectral location and efficiency of the luminescence are not borne out by experiment.(7) With regard to the dependence of efficiency on activator concentration, it should be pointed out that the Johnson–Williams "general treatment" is a special case which may be valid in particular systems, but which ignores completely effects which are expected, in many systems, to be of much greater importance than those which may be explained by a reduction in the thermal activation energy.(8)

In reply to Mr. Ewles, the initial increase of quantum efficiency with activator concentration may be accounted for in any theory of concentration quenching, by incorporating a term for competing absorption due to non-luminescent centres of any kind, such as the lattice itself, lattice defects, or non-activating impurities. It is therefore no evidence for the correctness of the concentration quenching theories of Ewles and Lee or of Johnson and Williams that they deduce this initial rise in quantum efficiency with activator concentration. Also, even in the absence of such competing absorptions, one obtains an initial rise in so-called "efficiency," if the "efficiency" considered is the number of quanta emitted per *incident* quantum of exciting light, rather than the true quantum efficiency. Unfortunately, most of the experimental data reported on inorganic phosphors relate to this "pseudo-efficiency," which is of no fundamental significance.

With regard to the large centre explanation of concentration quenching, it is clear from a theoretical point of view that in many systems sufficient interaction exists among isolated centres, i.e. single activator atoms, to allow energy transfer, but in which other measurable characteristics of the centres are not appreciably changed. Thus it seems that in these cases the "most obvious explanation" of effects at low concentrations is to be sought in terms of transfer phenomena.

In reply to Dr. Botden, the characterization of activator ions as "paired," "clustered" or "aggregated" does not imply to us that they are situated on adjacent cation sites. When, regardless of their separation, interaction between activation ions becomes so strong as to cause the appearance of a new absorption (or emission) band rather than merely to change the original band widths or decay constants, it seems reasonable to consider the interacting ions "paired" or "aggregated," i.e. as forming a new type of centre different from the "singlet" ions, which interact much less strongly with each other.

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Paper 13

Energy transfers in the calcium halophosphate phosphors

By G. R. FONDA, Dr.Ing., General Electric Co., Schenectady, N.Y., U.S.A.

Measurements have been made at temperatures of 87–475° K of the quantum output and efficiency of calcium fluorophosphate phosphors activated with variable concentrations of antimony and manganese. For antimony alone, the efficiency is greater and the temperature sensitivity is less when its concentration is so low that the luminous emission has a greater probability of arising from a primary, excited centre than from a centre which has received its excitation by successive transfer steps of resonance energy.

Consideration of the relative probability of these two types of emission serves to explain the greater output of manganese emission with increase in the concentration of either antimony or manganese, as well as the lower temperature sensitivity of the manganese emission.

Not only does immediate emission from the excited centre prove to be a more efficient process than emission which follows a resonance transfer, but the sensitized emission of manganese is found to be more efficient when it occurs as a direct transfer from a sensitizer to an activator centre than when it follows a succession of transfer steps.

There is a growing number of phosphors which exhibit sensitized luminescence.(1) Such a phosphor contains two activator elements. One, the activator proper, is responsible for the main emission band; it has no absorption band in the spectral range desired for excitation and consequently shows no fluorescence under radiation by light of that wavelength. The other element, the sensitizer, serves to introduce an absorption band at the desired location.

Some of the excitation energy absorbed by the sensitizer is transferred to the activator and reappears as light in an emission band characteristic of the latter. The fluorescence of the phosphor is a composite one and includes the emission bands of both elements at relative intensities which depend upon their concentration. In all cases so far studied, the emission band of the sensitizer is at a shorter wavelength than that of the activator.

It is believed that the transfer of energy from sensitizer to activator proceeds by a resonance process. In order for this transfer to occur in the calcium silicate phosphor containing lead as sensitizer and manganese as activator, Botden and

Kröger[2] at first assumed that the atoms of sensitizer and activator tend to arrange themselves in pairs at adjoining cation sites of the crystal lattice. This view has now been broadened to admit the possibility of transfer over a wider range. In studies on the relation between absorption and activator concentration for the same phosphor, Schulman, Ginther and Klick[3] found evidence that a direct transfer of excitation energy may occur from a lead ion to a manganese ion that is situated at any one of the neighbouring 28 cation sites.

Botden[1] admitted the occurrence of this direct transfer and, on the basis of different data, he calculated a value of 30. In addition, he found grounds for believing that sensitization may also occur by transfer of energy from one sensitizer ion to another, provided the latter is at any one of the 150 cation sites about the first. In such a case, a final transfer may occur to an activator ion in the manner of the direct transfer.

Botden's analysis has been extended by Dexter.[4]

CALCIUM FLUOROPHOSPHATE PHOSPHORS

Aim of investigation. The studies mentioned above have proposed that excitation energy of a sensitizer centre may be transferred to an activator centre in two ways, either as a direct transfer, or, when the activator centre is too remote, as a step-wise transfer through the medium of intervening sensitizer centres.

The further questions remain, what losses of excitation energy occur during these transfer steps and how are these losses dependent upon the relative concentrations of sensitizer and activator. Data have accumulated that furnish information on these questions for the calcium halophosphate phosphors.

Character and preparation of phosphors. The development of these phosphors has been described by Jenkins, McKeag and Ranby.[5] Further characteristics have been given by Butler and Jerome.[6] They exhibit the composition and structure of the mineral, apatite, $3Ca_3(PO_4)_2 . Ca(F, Cl)_2$. Antimony is added as the sensitizer element; it serves also to contribute a luminous emission band in the blue region. Manganese is the activator and its emission lies in the orange region. The colour of their combined fluorescence may be altered in two ways, by changing their relative concentration or by increasing the ratio of chlorine to fluorine and thereby shifting the manganese band further towards the red region.

Inasmuch as variable losses of chlorine are liable to occur during the firing operation, the phosphors for this investigation were made of the fluoroapatite, to ensure that their basic composition remained the same throughout.

A standard mixture was used which had these proportions:

$CaHPO_4 . nH_2O$	135·0 g
$CaCO_3$	43·8 g
CaF_2	11·4 g

After additions of antimony as Sb_2O_3 and of manganese as $NH_4MnPO_4 . H_2O$, samples were fired for one hour at 1180° C in long quartz test tubes whose open ends, projecting from the furnace, were plugged with glass wool. The composition of the final product approximated to the apatite formulation, $3Ca_3(PO_4)_2 . CaF_2$, in which substitution for some of the calcium had been made by antimony and by manganese.

The concentrations of the activators are expressed as percentages by weight of the fluorophosphate formed. No loss of manganese occurred during firing nor was there a loss of antimony within the range of concentration studied.

Absorption and emission measurements. Antimony introduces an absorption band in the range covering 2537 Å, the wavelength chosen for excitation of the phosphors. There is no absorption due to manganese within this range. The magnitude of the absorption band varies with the concentration of antimony to the extent disclosed by the reflectance curves of Fig. 1.

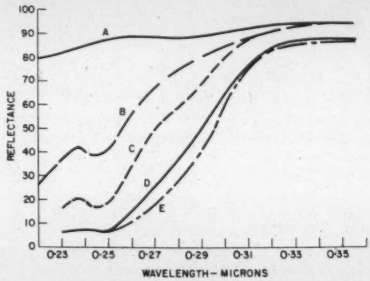

Fig. 1. Reflectance (%) of calcium fluorophosphate activated with antimony only

A, no Sb; *B*, 0·05% Sb; *C*, 0·19% Sb; *D*, 1·00% antimony; *E*, 1·10% antimony.

The spectral position of the antimony emission band varies only slightly with the concentration of antimony. At room temperature its peak location changes from 4780 Å at 0·05% Sb to 4850 Å at 1·0% Sb. It is, however, shifted very extensively to shorter wavelengths by an increase in temperature. Its peak location ranges from about 5100 Å at 87° K to about 4350 Å at 475° K.[7]

The manganese emission is much less susceptible to these changes. At room temperature its peak lies at about 5730 Å for the range of 0·5–3·7% Mn. Increase in temperature brings about a slight shift, again to shorter wavelengths, ranging from about 5850 Å at 87° K to 5640 Å at 475° K.[7]

In the present investigation, the interest lay in determining how the quantum output and efficiency are affected by changes in concentration of antimony and manganese, and by changes in temperature. Spectral emission curves of the emission were taken over a wide range in temperature under excitation by radiation having wavelength 2537 Å and under such controlled conditions that the data might be a measure of the relative output of the various phosphors.

The quantum output was calculated from the relative spectral distribution curves by integrating the product of intensity and wavelength over the range of 3900–7000 Å. At these limiting wavelengths the emission had fallen to negligible values. The outputs thus obtained are expressed as percentages of the output of magnesium tungstate measured under the same conditions. This percentage is referred to as the quantum output with reference to magnesium tungstate, whose quantum efficiency is reported as unity.[8] Division of the quantum output of a phosphor by its absorption for radiation having wavelength 2537 Å, taken from the curves of Fig. 1, gives its quantum efficiency as a percentage of that of magnesium tungstate.

ENERGY TRANSFER BETWEEN ANTIMONY CENTRES

Measurements. Curves for the variation of output with antimony concentration and temperature are given in Fig. 2.

Data for quantum efficiency at room temperature are given in Table 1, as related to the amount of antimony retained in soluble form after firing.

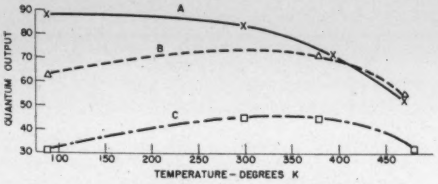

Fig. 2. Change in quantum output with temperature of calcium fluorophosphate activated with antimony only *A*, 1·00% Sb; *B*, 0·19% Sb; *C*, 0·05% Sb.

Table 1. *Quantum output and efficiency at 25° C of phosphors containing antimony only*

Sb (%)		Ca atoms per atom of	Absorption at 2537 Å	Quantum output	Quantum efficiency
Introduced	*Retained*	*retained Sb*	(%)	(%)	(%)
0·05	0·05	2400	52	45	87
0·20	0·19	640	76	73	96
1·00	1·00	120	90	84	90

At a concentration of 1·0% Sb, the output decreases with increase in temperature from 87° K upwards. Above room temperature, it falls off rather abruptly. With 0·05–0·20% Sb, however, the output increases considerably from 87° K to room temperature and does not begin to decrease until about 400° K. Because of the lower absorption of these phosphors, the quantum efficiency at 0·20% Sb is actually higher than that exhibited by phosphors made with 1% Sb.

Discussion. The high quantum efficiency and the greater uniformity of output with change in temperature that characterize phosphors low in antimony denote a direct release of excitation energy in the form of luminescence from excited centres without the intermediate step of a resonance transfer. This is a consequence of the greater separation of antimony centres.

Each centre presumably has as its kernel a single antimony ion. It represents a localized area of absorption to 2537 Å radiation. The total absorption recorded for a mass of phosphor crystals is the summation of the absorption of each individual centre.

In general, after a centre has been excited by the absorption of a photon of radiation having wavelength 2537 Å, its energy content is released in one or more of these three ways: (1) by direct emission as a quantum of luminescence energy; (2) by transfer to an adjoining centre and sensitization of the latter; and (3) by dissipation as a radiationless transition.

When the concentration of antimony is sufficiently high to allow appreciable transfer, then the probability of dissipation is increased proportionally to the number of centres that participate in the transfer before a luminous transition occurs. The efficiency for the output of luminescence is correspondingly reduced. This effect is noticeable for phosphors containing 1% Sb. The data of Table 1 show that each antimony atom at this concentration is surrounded on the average by 120 sites occupied by calcium atoms. An appreciable number of antimony atoms will therefore have another antimony atom as a neighbour at one of the surrounding 150 cation sites calculated by Botden as the limiting range for this type of transfer.[1]

When, on the other hand, the concentration of antimony is so low that the probability of transfer decreases appreciably, then the probability for direct emission from an excited centre is correspondingly increased, and the energy loss due to cumulative dissipations is to that extent reduced.

This explains the higher quantum efficiency of phosphors with 0·05–0·20% Sb and their better maintenance in output with increase in temperature. Each antimony atom at a concentration of 0·19% Sb is surrounded, on the average, by 640 calcium atoms, considerably more than the 150 calculated by Botden as the limiting range for appreciable transfer. The fact, incidentally, that the luminous output should increase in the temperature range of 87–300° K implies a low thermal activation energy.

ENERGY TRANSFER FROM ANTIMONY TO MANGANESE CENTRES

An understanding of the results will be clarified if the conclusion is kept in mind that was derived from the data on phosphors containing antimony; namely, that the highest efficiency is apt to be attained when the luminous transition takes place directly from an excited centre, a situation that results when the activator centres are so remote from one another that the probability is low for the transfer of excitation energy from one centre to another. The transfer of energy furnishes an opportunity for cumulative losses in the form of radiationless transitions and thereby lowers the efficiency.

The importance of this conclusion is shown by the efficiency measurements of Table 2 on phosphors containing a uniform amount of manganese, 0·9%, and variable antimony. As before, the efficiency is expressed as the percentage of the efficiency of magnesium tungstate. For the phosphors with manganese, the efficiency is based, of course, on the combined emissive output from manganese and antimony centres. The absorption of radiation having wavelength 2537 Å is unaffected by the presence of manganese.

Table 2. *Quantum efficiency at 25° C of phosphors containing variable antimony, with and without 0·9% manganese*

Antimony (%)		Ca atoms per atom of	Quantum efficiency (%)	
Introduced	*Retained*	*retained Sb*	*0·9% Mn*	*No Mn*
0·05	0·05	2400	52	87
0·20	0·19	640	68	96
1·00	1·00	120	76	90

The high efficiency that is characteristic of low antimony is lost in the presence of 0·9% Mn. This amount of manganese is such that each manganese atom is surrounded, on the average, by 60 cation sites. Even at such low concentrations as 0·05–0·19% Sb, transfer of excitation energy has taken place from antimony to manganese and a consequence of this has been partial dissipation of energy. The extent to which the transfer is utilized in sensitizing manganese centres is given by the data of Table 3. The quantum output in the absence of manganese is taken from Table 1. The decrease in the quantum output of antimony produced by the presence of manganese represents the amount of excitation energy undergoing transfer.

The decrease in output of antimony emission due to the presence of manganese represents the sum of the excitation energy transferred to manganese centres and that lost in radiationless transitions in the course of the transfer. The ratio given in the final column is a measure of the efficiency of transfer.

Table 3. *Dependence of energy transfer in phosphors containing 0·9% manganese upon concentration of antimony*

Sb (%) retained	*Ca atoms per atom of retained Sb*	*Quantum output (%) No Mn Sb only*	*0·9% Mn Sb*	*Mn*	*Decrease in Sb output (%)*	*Ratio Mn output to Sb decrease*
0·05	2400	45	17	10	28	0·36
0·19	640	73	32	19	41	0·46
1·00	120	84	35	33	49	0·68

That appreciable transfer should occur at such low concentrations as 0·05–0·19% Sb is in accord with Dexter's conclusion[4] that transfer may also occur over greater distances than those calculated by Botden. The very low efficiency of these transfers denotes high cumulative losses in the form of radiationless transitions. The improvement in efficiency with increase in the concentration of antimony is to be ascribed therefore to reductions in the number of transfer steps.

Phosphors were also prepared with 1·0% Sb and variable manganese. Data on them are given in Table 4.

Table 4. *Quantum output at 25° C of phosphors containing 1% antimony and variable manganese*

% Mn	*Ca atoms per atom of Mn*	*Quantum output (%) Sb*	*Mn*	*Sb + Mn*
0·0		84	—	84
0·5	107	58	18	76
0·9	60	35	33	68
1·8	29	13	49	62

The effect of varying the concentration of manganese is manifested in the following two ways:

(1) An increase in manganese concentration is accompanied by a decrease in antimony emission and by an increase in manganese emission. The concentration of the antimony centres is such that each is surrounded, on the average, by 120 cation sites, within the 150 calculated by Botden as the limiting range for appreciable transfer between sensitizer centres. In the absence of manganese, a fair proportion of the energy appears as direct emission from excited antimony centres. In the presence of manganese, however, the probability of transfer is increased proportionally to the manganese content. The increase in manganese emission is therefore accompanied by a decrease in antimony emission.

(2) The second effect is to lower the total quantum output. The combined output of antimony and manganese emission is less than the output for antimony in the absence of manganese. This again is a manifestation of the inherently lower efficiency associated with the transfer of excitation energy, and is a consequence of the cumulative dissipations during transfer.

The output of these phosphors was measured at various temperatures. The curves of Fig. 3 summarize the results. They are given also in Table 5, expressed as percentages of the quantum output at 25° C.

The decrease in antimony emission with rise in temperature is about as rapid in the presence of manganese as in its absence. This is in contrast to the behaviour of manganese emission, which is much more constant until a high concentration is reached. Such a result denotes that at temperatures

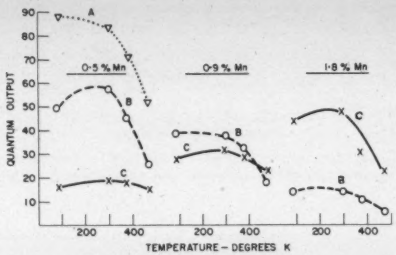

Fig. 3. Change in quantum output with temperature of calcium fluorophosphate activated with 1% antimony and variable manganese

A, antimony output in absence of manganese;
B, antimony output in presence of manganese;
C, manganese output.

Table 5. *Relative change in output with temperature for phosphors containing 1% antimony and variable manganese*

Temp.	*Relative intensity Sb output (%) No Mn*	*0·5% Mn*	*0·9% Mn*	*1·8% Mn*	*Relative intensity Mn output (%) 0·5% Mn*	*0·9% Mn*	*1·8% Mn*
87°K	105	87	101	98	85	87	91
298	100	100	100	100	100	100	100
378	84	79	86	71	93	92	64
473	62	44	48	40	80	73	48

above 25° C excitation energy is transferred preferentially to manganese centres before the extensive dissipation processes can arise which are characteristic of antimony centres at high temperatures. This suggests that above 25° C direct transfer from a sensitizer to an activator centre may occur over a greater distance than at 25° C or below.

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DISCUSSION

Dr. T. P. J. Botden: (*a*) For low Sb concentrations the absorption for 2537 Å radiation will increase at higher temperatures, since the absorption edge shifts to longer wavelengths and 2537 Å is situated on the absorption edge. When the temperature dependence curves of Fig. 2 are corrected for this change in absorption, it may well be that for low Sb content also the quantum efficiency is independent of temperature up to about 300° K. It is therefore not correct to speak of a low activation energy.

(*b*) The increase of the efficiency of energy transfer with higher Sb concentrations (Table 3) has been ascribed to the energy transfer. Since sensitizer-sensitizer transfer will exist both in Sb and in Sb, Mn-activated phosphors, and the quantum efficiency of Sb-activated phosphors is high, the

rather high loss in the total quantum efficiency in Sb, Mn-activated phosphors must be caused by quenching centres brought into the crystals by the incorporation of Mn. Consequently the efficiency of the Sb emission in Sb and Sb, Mn-activated phosphors cannot be compared in order to calculate the efficiency of transfer, and it cannot be concluded from the data of Table 3 that Sb–Sb transfer results over longer distances than those covered by 150 cations.

Dr. W. L. Wanmaker: The efficiency of a phosphor layer in a fluorescent lamp is largely dependent on the absorption of ultra-violet radiation, which for halophosphates is determined by the antimony content; in general the absorption is rather low for these phosphors, and it is important to increase it. Dr. Fonda states that the quantum efficiency of fluoroapatites decreases with increasing Sb content, but does the same hold for commercially used fluorochloroapatites?

Samples of the latter were made with an estimated quantum efficiency of 90%. At 0·9% Mn content, a sample with 1·5% Sb gave 62·8 lm/W at 0 hour in a lamp, and another with 1·17% Sb gave 64·5 lm/W at 0 hour. The colour temperature of the lamps was 4200° K. Fonda's corresponding fluoroapatite with 0·9% Mn and 1·0% Sb had a quantum output of 68% at 25° C, which suggests that the quantum efficiency of the F–Cl powders is not so strongly dependent on the Sb content as for fluoroapatites.

Dr. S. Rothschild: Dr. Fonda mentioned that in sensitized luminescence the emission band of the sensitizer is always at a shorter wavelength than the emission of the activator. But SrS.Pb, Pr phosphors with Na_2SO_4 as flux show the red Pr emission at 6300–6400 Å and the green Pr emission at 5120–5220 Å, with the Pb emission peaked at 5400 Å in between.(1) The position of the emission band is in itself quite irrelevant to the sensitization process. It is even conceivable that certain sensitizers do not emit at all, possible examples being CaS.Pb phosphors sensitized by the introduction of 2% CdS into the lattice.(2) The addition of CdS causes a strong long-wavelength absorption.

Mr. J. Ewles: Dr. Fonda suggested that with increasing Sb concentration the probability of radiationless dissipation is greater. Yet in Table 1 the efficiency is greater for 1·0% Sb than for 0·05%.

Also in Table 3 the efficiency of transfer from Sb to Mn is greater with greater Sb content, whereas according to Fonda's arguments it should be less.

In both cases the efficiency of emission of Sb per Sb ion and the efficiency of transfer per Sb ion does indeed decrease with increasing Sb concentration.

Author's reply: At an optimum concentration of Cl, my measurements have given a quantum efficiency for Sb + Mn of 88%, close to Dr. Wanmaker's estimated value of 90%, and considerably above the value of 76% from Table 3 for the fluoroapatite. For an all chloroapatite, I have obtained a value of 51%. Whether these effects are due to changes in 2537 Å absorption or in the efficiency of the luminescence process, seems still an open question.

Concerning Mr. Ewles' contribution, the greater prevalence of radiationless transitions in the absence of Mn and above a critical concentration of Sb was suggested because of the optimum shown in Table 1 for 0·20% Sb. The poorer efficiency at 0·05% Sb seems due to greater absorption of emitted luminescence with such very dilute Sb. In the presence of Mn, the improvement in efficiency for Sb + Mn that occurs with increase in Sb, as recorded in Table 1, was ascribed in the paper to reduction in the distance of Sb–Mn transfer steps.

The alternative opinion expressed by Dr. Botden deserves serious consideration and demonstrates the need for further experimental data. His comments on possible changes in absorption with temperature are also helpful.

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Paper 14

Divalent manganese as a luminescent centre

By C. C. KLICK, Sc.D., Naval Research Laboratory, Washington, D.C., U.S.A.

Current information concerning the luminescence of divalent manganese is reviewed. Recent experimental and theoretical investigations indicate that the excited state leading to emission has four of the 3d electrons with parallel spins and one anti-parallel, while the ground state has all electrons with parallel spins. Configuration co-ordinate curve calculations from experiment show that there is little lattice relaxation around the manganese ion after optical transitions. This has led to one explanation of the asymmetric emission band characteristic of divalent manganese in terms of transitions to discrete vibrational levels of the ground state. Another widely proposed explanation is that there are various sub-bands in the emission spectrum coming from close-lying electronic states of the ion. Auxiliary experiments have thus far failed to decide between these views. In silicate type phosphors both red and green emission bands arise from divalent manganese. Two explanations have been offered for these bands. One, the "cluster" theory, is that each band corresponds either to a single ion or cluster of ions. The other, the "co-ordination" theory, is that the colour is primarily dependent on the number of ions surrounding the activator. Recent experiments on the concentration dependence and magnetic properties of manganese-activated silicate phosphors tend to support the latter explanation.

Divalent manganese as a luminescent centre has been of widespread interest both because of its presence in a large number of commercially important phosphors and because of its unusual properties. Among these are its long decay time, its asymmetrical emission in zinc silicate, the appearance of at least two emission bands in silicate phosphors, and the ability of manganese to luminesce in a wide variety of host lattices. In this paper some of the more recent information concerning the nature of this centre is reviewed.

MANGANESE ENERGY LEVELS INVOLVED IN LUMINESCENCE

It has been observed that there is a long, temperature-independent decay of luminescence from divalent manganese centres and that this luminescence is not associated with photoconductivity. These facts, along with the poor optical absorption in the manganese ions, has led to the general conclusion that the optical transition leading to luminescence is a forbidden one. Further detailed analysis of the nature of the centre was handicapped because the atomic spectrum of divalent manganese was not analysed until quite recently.

From consideration of the energy involved in the emission spectrum, however, Kröger[1] concluded that the energy levels involved in absorption and emission must have the same principal quantum number. By analogy with the atomic spectrum of trivalent chromium, which is similar to divalent manganese in electronic configuration and optical properties, Kröger further concluded that the ground state level was a ^6S term and that the excited states are to be found in the Stark levels of the ^4G, ^4D, ^4P, and ^4F terms.

Johnson and Williams[2] measured the magnetic moment of manganese-activated zinc fluoride and found that it decreased when the phosphor was excited. This was interpreted as being due to a change in multiplicity of the luminescent centre and is in agreement with the suggestion of Kröger that the ground state is six-fold degenerate and the excited state four-fold degenerate.

Catalán and Garciá-Riquelme[3] have recently published the energy level scheme of doubly ionized manganese and the energy levels are ^6S, ^4G, ^4P, ^4D, and ^4F starting with the lowest term. The energy difference between the ^6S and ^4G state is 3·32 electron volts.

Ginther[4] found a detailed excitation spectrum for divalent manganese in K_4MnCl_6 and Klick and Schulman[5] found very similar spectra in absorption and excitation measurements on $MnCl_2$. The presence of as many as nine absorption bands for divalent manganese is an indication that in solids the manganese ion retains many of the characteristics of its atomic spectrum. Furthermore, it was suggested[5] that the lowest excited levels of the manganese ion have their orbital angular momentum quenched since both theory[6] and experiment[7] on magnetic ion salts indicate this to be the case.

The result of these investigations, then, seems to be that the lowest excited state, from which the luminescent transition occurs, differs from the ground state only in its multiplicity, with no change in principal quantum number or orbital angular momentum. In the ground state the divalent manganese ion has all five of its 3d electrons alined with spins parallel; the first excited state has four parallel and one anti-parallel. Williams[8] has calculated theoretically the emission of divalent manganese in potassium chloride and has also concluded that a change of spin of one electron is involved in the emission process. Thus, there appears to be general agreement concerning the mechanism involved in the luminescence of divalent manganese.

ASYMMETRICAL EMISSION BAND OF DIVALENT MANGANESE

It has long been known[9] that the emission spectrum of manganese-activated zinc silicate is not symmetrical but possesses a long wavelength tail. Attempts to account for this phenomenon have led to considerable discussion.

A number of workers[10–14] have suggested that the emission consists of several overlapping emission bands which cannot be individually resolved in the usual way. To find the location and intensity of these sub-bands the observed emission spectrum is analysed into a series of Gaussian curves of varying location and height such that their sum is the observed curve. Each of the Gaussian curves so found is then considered to correspond to an individual emission band.

The justification for this procedure rests both on experimental and theoretical grounds. From the experimental point of view it has been shown[10, 13] that a number of simple phosphors possess an emission spectrum which is closely Gaussian. The phosphors most closely investigated have been the tungstates and these seem to fit a Gaussian curve better when the spectrum is plotted as intensity *versus*

wave number, rather than number of emitted quanta *versus* wave number.

Theoretically, a simple model of a luminescent centre based on configuration co-ordinate curves also predicts an approximate Gaussian emission spectrum. Schön[15] suggested that luminescent centres possess a zero point vibrational energy, and measurements on the low temperature luminescence properties of a variety of materials[16, 17] confirm this view. From this starting-point a semi-classical model of the luminescent centre has been developed[17–19] which treats it as a simple harmonic oscillator with equally spaced vibrational energy levels and a zero point vibration which prevents the low temperature emission and absorption spectra from becoming line spectra. The approximations involved in this model have been investigated by Williams and Hebb[20] and by Lax.[21] Using this model, let us consider a luminescent transition at low temperatures. At sufficiently low temperatures (less than 50° K in most cases) most of the excited luminescent centres will exist in their lowest vibrational state before luminescing. The probability distribution of a harmonic oscillator in this vibrational state as a function of displacement is Gaussian. If the transition is to a portion of the ground state configuration co-ordinate curve which is many vibrational quanta above the minimum of the curve, the curve may be treated classically by the correspondence principle.[20] In cases where the portion of the ground state curve to which transitions are made is a straight line, the emission spectrum would be expected to approximate to a Gaussian curve.

When applied to the emission of divalent manganese in zinc silicate, the Gaussian analysis yields two or more bands. Attempts, however, to find properties of these bands which vary so that the bands might be separated experimentally have not been successful. Klick and Schulman[22] failed to find more than one emission peak at 4° K. They also failed to find a variation in emission spectrum with the time interval between the stopping of excitation and the measurement of the phosphorescence,[22, 23] although such a change has been reported by Nagy.[24] Also, Oszy[25] failed to find any phenomena in the excitation spectrum which might suggest more than one band. Finally, the variation of band width with temperature is regular[5] and indicates a single vibrational frequency for the excited manganese ion before luminescence occurs.

As pointed out above, the justification for a Gaussian analysis of the emission spectrum is strongest when transitions are to a portion of the ground state curve many vibrational levels above the equilibrium value. Only under these conditions is it permissible to treat the ground state as a classical configuration co-ordinate curve. In the case where there is little shift of the configuration co-ordinate curves in going from the ground to the excited state, luminescent transitions are to low-lying, vibrational levels of the ground state and the emission probabilities must be computed using wave functions for both the initial and final state. It is simple to determine experimentally when such a case occurs, for then the energy separation of the peaks of the absorption and emission bands is small; few vibrational quanta are emitted. That this is the case for divalent manganese is evident from the data on K_4MnCl_6, $MnCl_2$, and Zn_2SiO_4 . Mn. For the last case there is a small excitation peak at about 4700 Å and the emission peak is approximately 5200 Å. These observations have led Klick and Schulman[5] to question the use of Gaussian analysis in this case. They computed configuration co-ordinate curves for divalent manganese in zinc silicate and concluded that the minima of the curves are shifted with respect to each other by less than 0·1 Å.[26]

As an alternative explanation of the asymmetrical emission of divalent manganese it was suggested[5] that this is normal behaviour for a system with vibrational levels and slightly shifted configuration co-ordinate curves. Transition probabilities computed for such a case gave points falling on a curve with a long wavelength tail. While, in principle, the vibrational levels should lead to a series of equally spaced emission lines, there appears to be sufficient "smearing out" in most cases so that this fine structure is not observed; this is presumed to be the case with manganese-activated materials. Qualitatively, the effect arises because the short wavelength extent of the low temperature emission is determined by the transition between the lowest vibrational level of the excited state and the lowest level of the ground state. No more energetic transition is possible. There is no such limitation on the long wavelength side so that an asymmetry may easily occur.

Should there be a phosphor in which the manganese emission maintained some of the fine structure suggested by this model, the arguments given above would be considerably strengthened. The author has failed to find such cases in emission measured at 4° K for manganese concentrations of 100 parts per million in cubic and hexagonal zinc sulphide and in zinc silicate. Other results for zinc silicate[27] are as yet unexplained, since the reported fine structure peaks are not equidistant and their average spacing corresponds to a frequency much less than that expected from configuration co-ordinate curves.

Unfortunately, then, experiment does not decide between these two explanations of the observed asymmetry in the manganese emission. It is the author's opinion that in cases such as that occurring in manganese, skewed rather than true Gaussian curves should be observed, and that this is shown by experiment on manganese luminescent centres. Should this view be correct, there may be only one excited state level and one ground state level involved in the emission process.

INFLUENCE OF ENVIRONMENT ON THE EMISSION SPECTRUM OF DIVALENT MANGANESE

In addition to analysing phosphors activated with divalent manganese to determine the nature of the transition and whether it results in single- or multiple-band emission, considerable work has been done on the determination of which environmental factors are most influential in determining the emission spectrum. In particular, the discussion has centred on cases in which oxygen ions surround the manganese and in which both "green" and "red" bands may appear.

The principal experimental facts are:

(*a*) At concentrations of manganese up to a few per cent in zinc silicate only the green band appears.

(*b*) At concentrations approaching 20% a red band develops in addition to the green band. In this case the phosphor does not luminesce at room temperature, but luminescence may be observed at liquid nitrogen temperatures.

(*c*) The addition of beryllium even at low manganese concentrations promotes the development of the red band and the effect increases with increased manganese concentration.

(*d*) In zinc germanate, a material structurally similar to zinc silicate, only a green band appears even at high manganese concentrations.

(*e*) The presence of beryllium in the manganese-activated zinc germanate produces a red band in addition to the green band. This new band increases with manganese concentration as in zinc silicate.

Two explanations have been given of these effects. The first is the "cluster" theory suggested briefly by Maurer[28] and Kröger[29] and elaborated in detail by Kröger and Zalm.[30] In this picture the different emission bands correspond to various size clusters of manganese ions; for example, the green band may be due to isolated ions and the red band to pairs consisting of an ion with another manganese ion in close proximity. A simple explanation of the increase of the red band with concentration is offered by the cluster theory since the relative number of clusters of activator ions increases with concentration assuming a random distribution. The influence of beryllium is accounted for by suggesting that manganese ions tend to cluster preferentially around beryllium ions. This is presumed to reduce the strain energy in the lattice arising from the ion size mismatch when zinc is replaced by manganese which is larger and beryllium which is smaller.

The "co-ordination" theory, proposed by Linwood and Weyl[31] and applied to the present problem by Schulman and others[32–35], argues that the green luminescent band arises from activator ions surrounded by four oxygen ions as when manganese replaces zinc substitutionally; the red band is presumed to arise when manganese is co-ordinated with six oxygen ions which occurs when the activator occupies an interstitial position. In this theory the effect of beryllium is thought to be to replace quadrivalent silicon or germanium ions in the lattice. Then, in order to maintain electrical neutrality, some divalent manganese ions find interstitial positions of six-fold co-ordination in the rather open lattice structure thus leading to the red band. The effect of manganese alone is for the manganese or zinc ions to perform the function ascribed to beryllium and again have manganese ions forced into interstitial positions. Because of the large ion sizes involved, this process occurs only at large manganese concentrations.

The summary given here of these two theories has been necessarily brief and does not give the full range of arguments which have been employed. Since, however, both these theories account reasonably well for the multi-band luminescence of the materials investigated, there have been attempts made to find experiments which would indicate more clearly which theory is to be preferred. One such attempt was made by Spencer and others[36] who measured the width of the paramagnetic resonance band of manganese in these materials and related the results to the clustering of manganese ions as proposed in the cluster theory. They found that with increasing manganese concentration the paramagnetic band width *decreased* while increasing beryllium concentrations *increased* the band width. The band width depends on three effects: dipole-dipole broadening, exchange narrowing, and, as Herschberger and Leifer[37] suggested for manganese-activated zinc silicate, anisotropic energy broadening. As paramagnetic ions, such as manganese ions, approach each other the dipole-dipole interaction tends to broaden the resonance spectrum while the exchange forces, in general becoming important at small distances of separation, tend to narrow it. An increase in anisotropy would be expected to increase the anisotropy broadening. If the decrease in band width of the resonance with increasing manganese is to be attributed to this effect, high concentrations of manganese must reduce the anisotropy. This might occur by having two paramagnetic ions interact so strongly that their spins become oriented in preferred crystallographic directions. Such an interaction would increase as distance between ions decreased. Thus all three effects should be sensitive to the formation of clusters. While it is not certain which of the effects is predominant, the significant result of this experiment is that increasing beryllium and manganese concentrations affect the clustering differently while the cluster theory postulates that the effect would be the same.

Leverenz and North[38] concluded from the concentration dependence of the decay constant, efficiency, and temperature break point that clusters of manganese ions are not important as luminescent centres in manganese-activated zinc silicate at room temperature. It would be interesting to extend these measurements to liquid nitrogen temperatures where the red band is much more prominent.

These experiments tend to argue against the cluster theory and it may at least tentatively be concluded that the red and green bands are primarily determined by the number of nearest neighbour oxygen ions.

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DISCUSSION

Mr. C. G. A. Hill: In connexion with the relation between the emission spectrum of manganese and its environment an interesting observation was made with calcium carbonate. In calcite, where the Ca^{2+} ion is 6-co-ordinated with oxygen, Fonda and Schulman have shown that the Mn emission is orange-red. In aragonite, where the calcium is 9-co-ordinated, we find a yellow-green emission. This shift is in the opposite direction to that expected from a simple extrapolation of the Linwood and Weyl hypothesis. On heating manganese-activated aragonite to 420° C it is transformed rapidly to calcite and the emission shifts to the same orange-red shown by precipitated calcite. It seems improbable that any clustering takes place during this transition.

Dr. S. T. Henderson: The work of Klasens and others[1] on manganese-activated perovskites suggests that the co-ordination number hypothesis cannot apply in its original form to fluorine-dominated lattices, and Smith[2] has produced similar evidence to the effect that the 6-co-ordinated fluorides show orange emission bands while the eightfold structures emit in the green region.

Mr. A. P. Rice: The assumptions made concerning the promotion of a red band by beryllium, in both the co-ordination and cluster theories of the emission of Mn^{2+}, cannot be directly verified. A different approach is proposed to the question of the origin of the "red" and "green" emissions in manganese-activated phosphors, having regard to the strong tendency of zinc phosphors to produce a green emission.

Similar green emissions are found in the β Al_2O_3 phosphors, which incorporate divalent ions (Ca^{2+}, etc.), and in $ZnAl_2O_4$ and $MgAl_2O_4$, all with manganese activation, when these systems are prepared under reducing conditions. Under oxidizing conditions, however, Kröger has stated that the $ZnAl_2O_4$ emission is unchanged, whereas $MgAl_2O_4$ develops an additional red emission band. By virtue of the dissociation of ZnO at high temperature, a tendency for either anion vacancies or interstitial Zn^+ ions to appear would be expected in zinc phosphors while in the β Al_2O_3 phosphors the divalent ions would produce anion vacancies. Further, the prior formation of $ZnMn_2O_4$ in the synthesis of Zn_2SiO_4 phosphors has been shown to produce specific luminescence effects, e.g. longer afterglow; thus the assumption of random distribution of activator ions may not be entirely valid. These considerations suggest that the green emission may be due to a specific interaction of the activator ion and some other species in the lattice, possibly an anion vacancy.

The red emission is qualitatively similar to that of the pure manganous halides in which there is a higher probability of Mn^{2+}–Mn^{2+} interactions. "Red" centres may thus appear in the absence of more powerful interactions of the type suggested for "green" centres. In the case of complex emissions in the 6400–7000 Å region, often suggested as due to Mn^{4+}, it may be significant that the phosphors concerned are predominantly magnesium compounds.

Dr. K. H. Butler: It is generally assumed that the probability distribution of position for the lowest vibrational states is Gaussian. If so, then "reflexion" of this in a curved portion of the potential energy curve of the normal state should give, not an asymmetrical spectral energy distribution, but rather one which deviates from the Gaussian distribution at both high and low frequency.

On Dr. Klick's theory it is also difficult to account for the increasing asymmetry as the manganese concentration increases, which can be accounted for if two or more components are actually present. The lack of direct experimental evidence for these may be due to an equilibrium among the excited states owing to their long lifetime.

Dr. G. Szigeti: The Gaussian form of emission bands may be regarded as a good approximation. The physical structure in a band is shown by the different decay constants for the components, e.g. in zinc orthosilicate, in the green $\sim 200\ sec^{-1}$, in the yellow $\sim 1800\ sec^{-1}$ and in the blue $\sim 72000\ sec^{-1}$.[3]

Dr. C. C. Vlam: The theoretical curve for the emission spectrum of manganese-activated zinc silicate, based on the configuration co-ordinate model, was compared with the measured low-temperature emission. The value of the force constant of the ground state of the centre was chosen so as to give the experimentally determined value of the activation energy, W. Near the minima the potential energy curves are parabolic, but near the point of intersection they will probably deviate from this form. It may therefore be doubted whether it is justifiable to use the W-value for the calculation of the potential energy curve.

The calculation shows the *o–o* transition to have the largest probability, and the computed points only determine the low-frequency wing (see Paper 14, reference 5). To account for the high-frequency slope of the emission one must assume the very improbable half-width of 200 Å for the separate lines, corresponding to transitions between the vibrational levels. Actually at low temperatures the emission spectrum shows a great number of separate though not equidistant narrow bands, with widths of approximately 10 Å. This irregular fine structure may arise from the presence of different excited states and vibrational modes, deviations from the parabolic form of the potential energy curves, and Stark splitting of the levels. The high-frequency slope requires the *o–o* transition to have a small probability, as in the case of the tungstates and KCl.Tl, and thus the X_0-value calculated by Klick will be larger, producing emission bands close to Gaussian form.

Author's reply: In reply to Mr. Rice, on the configuration co-ordinate model the absence of interaction of an activator with its surroundings would lead to resonance radiation. As the interaction with the crystal increases a Stokes shift is observed and the amount of this shift determines the colour

of the luminescence. This interaction is influenced by the presence of foreign ions, lattice defects, other activator ions, the number of neighbours, distance of the neighbours, and symmetry of the lattice. Our knowledge of these interactions is still primitive and this review has attempted to compare the importance of only two of these interactions in the case of a single activator for a special class of materials. Attempts, such as those mentioned by Rice, to look into other interactions and other materials should prove most informative.

In reply to Dr. Butler, the portion of the configuration co-ordinate curve which is appreciably curved is near the minimum. As pointed out in the paper, transitions in this case need to be computed, not from the classical curve, but using the wave equations of the vibrational levels involved. This leads to a series of lines which may be broadened out to appear continuous. In this picture the apparent Gaussian shape of the short wavelength side of the emission spectrum in Zn_2SiO_4. Mn is then determined primarily by the broadening of the luminescence corresponding to the most energetic transition.

On the multiple band model of manganese luminescence, the effect of increasing manganese concentration would presumably be ascribed to a change in transition probabilities induced by the nearness of one manganese activator to another. On the single band model the effect would be ascribed to changes in the configuration co-ordinate curves of a manganese activator near another manganese ion. These two explanations are essentially similar.

With regard to Dr. Szigeti's comments, the blue luminescence referred to appeared even in samples with no manganese and was gradually suppressed by increasing concentration of manganese so that it was not found in samples with 0·8% manganese.[4] This suggests that the blue luminescence was characteristic of the host lattice rather than of the activator. It has also been suggested[5] that the yellow bands were due to the presence of a β-willemite phase resulting from a 0·9 mole of excess silica used in the preparation of these samples.

The faint fine structure in the willemite emission, observed by Dr. Vlam, remains one of the puzzling properties of this material and may prove to be most informative when completely understood.

The luminescent transition may not be to a point high on the side of the ground state configuration co-ordinate curve, as Dr. Vlam suggests. In Zn_2SiO_4. Mn the first manganese absorption band occurs in the vicinity of 4800 Å and the emission peaks at 5200 Å. The energy difference between these values corresponds to a Stokes shift of 0·2 eV which is the energy of five vibrational quanta at a frequency of 10^{13} c/s. Since the Stokes shift includes the relaxation energy in both absorption and emission, the number of vibrational quanta given off in either transition must be small and the transitions must be close to the minima of the configuration co-ordinate curves.

With regard to the width of emission "lines" in solids, the case of the edge emission in CdS may be considered. For pure single crystals of this material the lines have a half-width of 10 Å while for the powdered phosphor prepared in the usual way the width is 50 to 100 Å.[6] It does not seem unreasonable, then, that a magnetic ion such as manganese used in the relatively high concentration range which is necessary should have lines broadened as much as 200 Å.

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Paper 15

Atomic configurations in luminescent centres

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When the activator ions in a phosphor have a charge different from that of any ions in the host lattice, it is generally agreed that charge compensation must take place. A new theory of luminescent centres is proposed in which the compensation of charge, by lattice vacancies or by activator ions, is localized in the vicinity of the activator ions. This theory is primarily applicable to ionic crystals, and specific configurations of lowest energy can be deduced. These configurations are described in detail for alkaline-earth oxide, uranate and fluoride phosphors. and the vibrations of these centres are discussed. A number of original phosphors of theoretical interest, including CaO . Bi, Li; CaO . U, Li; CaO . U, Sm; and the uranates, are described and spectra are shown. Finally, necessary modifications of the present theories of sensitized luminescence and multiple-band emission are considered.

There is a good understanding of the nature of the luminescent centres in some of those phosphors in which an activator ion replaces a lattice ion of the same charge. In particular, Williams[1] and others have intensively studied KCl.Tl, which is a phosphor of this type. However, when the activator ions have an ionic charge different from that of the lattice ions, there has been no general agreement as to the specific atomic configurations in the luminescent centres. Kröger[2] and others have stressed that charge compensation must take place, and have applied this idea to the theory of the sulphide phosphors. In the most important examples of this class of phosphor a single ion compensates each activator ion, and the dissociation of the ion pairs has been thought to be considerable[2] due to the high dielectric constant of the sulphides. The results obtained by Kröger and Dikhoff[3] on ZnS.Pr, Cu or Ag indicate otherwise, as they found distinct changes in the line intensities depending on the choice of monovalent ion; but the interpretation of the sulphide phosphors is particularly difficult owing to the partly covalent nature of the interatomic bonds.

The present theory of luminescent centres is an extension of the idea of compensation of charge, and it is now proposed

that in ionic crystals the compensation of charge, taking place either by lattice vacancies or by compensator ions, is localized and occurs without any ions being in interstitial positions. The degree of dissociation of the ions in the centre is expected to be small in most ionic crystals, and especially so in cubic crystals of the RX type, e.g. CaO, where both the shortest distance between positive ions and the dielectric constant are moderately small. Large excess charges and low temperatures will also favour the stability of the centres.

Interesting configurations of the activator ions, and of the compensator ions or vacancies, can be expected to occur when there is an excess charge on the activator ion; and the configuration of lowest energy should provide an adequate description of the centre. Two or more centres may combine and such a group will be called a "cluster," this being in rough conformity to the previous usage.

Although luminescent centres appear to offer the greatest variety of configurations, a few examples have been described in other branches of solid-state physics. Seitz[4] has suggested that in the alkali halides, positive and negative ion vacancies will tend to form neutral pairs, as will also a divalent positive ion and a positive ion vacancy; and he has discussed the formation of groups of such pairs, e.g. the weak aggregation of two pairs of divalent ions with associated vacancies. Reitz and Gammel[5] have calculated that the binding energy of the cadmium ion and a positive ion vacancy in NaCl is 0·44 eV. This is in fairly good agreement with the value of 0·3 eV experimentally determined by Etzel and Maurer,[6] and supports the idea of local charge compensation. Verwey[7] and others have also given examples of charge compensation in their treatment of semiconductors, e.g. the association of a Cu^{2+} ion and a positive ion vacancy in Cu_2O at low temperatures.

The groups of ions in a centre or cluster will have a characteristic set of vibrations, which in favourable cases may have an observable effect on the absorption and emission of the phosphors. The negative ions in the vicinity of the activator must be included in the description of the centre, especially when considering the possible vibrations.

ATOMIC CONFIGURATIONS IN OXIDE PHOSPHORS

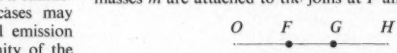
The configurations of lowest energy will now be considered for a trivalent, tetravalent or hexavalent activator ion in a face-centred cubic crystal of the RX type, when there is compensation either (*a*) by lattice vacancies due to missing divalent positive ions or (*b*) by the replacement of divalent positive ions by monovalent positive ions. Calculations of the potential energy of possible configurations have been made, to decide in doubtful cases which is the configuration of lowest energy. Only the coulomb energy terms have been included in these rough calculations, but in most cases the configuration of lowest energy is obvious. It would be possible to calculate the energy of dissociation of these configurations by the Mott–Littleton[8] method, which includes displacement and polarization terms, in the same way as Reitz and Gammel,[5] and later Bassani and Fumi,[9] calculated the energy of dissociation of a Cd^{2+} ion and a lattice vacancy in NaCl, but such calculations have not yet been performed.

Case 1. *A trivalent ion.* (*a*) The activator ion, *A*, has one unit of excess positive charge beyond the charge normally present in the crystal lattice, whereas a positive ion lattice vacancy denoted by *D* is equivalent to an excess of two units of negative charge. Hence the simplest way of achieving electrical neutrality is for one lattice vacancy to be associated with two activator ions. The configuration of lowest energy is that of a linear electric quadrupole with the lattice vacancy midway between the two activator ions, i.e. *A D A*, and the orientation will be along the direction for which positive ions are closest together, i.e. the [110] direction for a face-centred cubic crystal. Examples of this type are CaO.Bi and MgO.Cr. It is an interesting feature of the theory of localized charge compensation that a centre may have to contain more than one activator ion in order that electrical neutrality can be achieved. The Bi ions have been shown to be trivalent in CaO.Bi using a chemical test described by Kröger and others.[10]

At liquid-air temperature, the CaO.Bi phosphor has a banded structure on the short wavelength side of 4300 Å, and it has been shown by Ewles[11] that the bands may be numerically represented by an electron vibration band-head formula of the type

$$\nu = \nu_0 + (v' + \tfrac{1}{2})w' - (v'' + \tfrac{1}{2})w''$$

where v' and v'' are small integers or zero, w' and w'' are frequencies of the vibrational order of magnitude $\simeq 500\ \mathrm{cm}^{-1}$ and ν_0 is the frequency of the electronic transition involved. Ewles has suggested that the electron vibration bands are associated with the host lattice; but it is now suggested that the vibrations are those of the two Bi ions in the centre. On this basis, there will be two main normal modes of vibration, the one in which the two Bi ions vibrate symmetrically towards the defect, i.e. $\rightarrow\ \leftarrow$ and a vibration in which the two ions are in phase, i.e. $\rightarrow\ \rightarrow$. A rough calculation can be made of the ratio of the values of the two vibrational frequencies, i.e. w''/w', using a mechanical analogy. If three similar stretched elastic strings are connected end to end between two fixed points *O* and *H*, and masses *m* are attached to the joins at *F* and *G*, thus



then the frequencies of the normal modes of vibration can be shown, using Lagrange's method for the solution of problems of small oscillations, to be in the ratio $\sqrt{3} : 1$, the symmetric mode having the larger frequency. The values found by Ewles for w' and w'' from an analysis of the CaO.Bi bands yield a ratio of 493 : 298 or 1·65, which is reasonably close to the value of 1·73 for the above simplified model.

Another example of a phosphor containing trivalent ions compensated by defects, is MgO.Cr, which is excited by cathode-rays. Deutschbein[12] has described the spectrum, which consists of broad lines and narrow bands. This spectrum is more complicated than that of CaO.Bi, due to the electronic transition occurring in an incomplete electron shell; but it is being restudied, along with phosphors of the the CaO.Sm type where the shielding is more complete, to determine whether the vibrations of the centre affect the emission.

Case 1(*b*). Compensation by a monovalent positive ion *C* is accomplished when one activator ion and one compensator ion are in neighbouring cation sites, i.e. *C A* along the [110] axis. However, there may be a reduction in energy when a cluster of two such centres is formed, i.e. $\begin{matrix} CA \\ AC \end{matrix}$. This is the formation of a quadrupole from two dipoles, and is similar to the configuration suggested by Seitz for divalent ions and vacancies in alkali halides. Examples of this type are the new phosphors CaO.Bi, Li, and MgO.Cr, Li.

The CaO.Bi, Li emission spectrum when excited by 3650 Å

radiation includes bands very similar to those for CaO.Bi and also a weak band in the red region in approximately the same position, near 6450 Å, as a band occurring in the CaO.Bi spectrum at high Bi concentrations. This emission is believed to be due to a Bi ion adjacent to another Bi ion. The specific configuration responsible for the emission of red radiation in CaO.Bi is probably a cluster containing two centres, i.e. $\begin{matrix} A\,D\,A \\ A\,D\,A \end{matrix}$, and the emission can be expected to be slightly different from that due to the similar cluster $\begin{matrix} C\,A \\ A\,C \end{matrix}$ occurring in the CaO.Bi, Li phosphor.

MgO.Cr, Li has also been investigated, and it is found that the lithium greatly enhances the deep red emission at room temperature under cathode-ray excitation.

valent ions are at the corners of a tetrahedron with the hexavalent ion at the centre, Fig. 2. The tetrahedron is not regular, but can be derived from a regular tetrahedron by stretching along one of the axes of two-fold rotational symmetry. A simple coulomb energy calculation indicates that the tetrahedral formation is very slightly the more stable. It is quite possible that both types of centre can occur in the phosphor. As no previous example of this type was known, it was decided to investigate CaO.U, Li and its liquid-air temperature emission spectrum when excited by 3650 Å radiation is shown, Fig. 1(*b*). This phosphor has a similar spectrum to CaO.U, but the differences in the line intensities are sufficient to suggest that some atoms very near to the U atoms are different. The CaO.U, Li phosphor is much brighter at room temperature than the CaO.U phosphor,

Fig. 1. (*a*) CaO (1% U) (10 min); (*b*) CaO (1% U, 4% Li) (10 min); (*c*) Ba_2CaUO_6 (10 min)

Figs. 1, 4, 6. The spectra were obtained with a Hilger medium quartz spectrograph using the Hartmann diaphragm. The slit width was 0·025 mm and the spectra have been enlarged × 3 (approx.). The exposure times are shown in brackets. Figs. 1 and 6 were obtained from Ilford Rapid Process Panchromatic Plates and Fig. 4 from an Ilford Long Range Spectrum Plate.

Case 2. *A tetravalent ion.* (*a*) Electrical neutrality is maintained by one lattice vacancy being associated with each activator ion, i.e. *DA* along the [110] axis. This type of centre will tend to form clusters, i.e. $\begin{matrix} D\,A \\ A\,D \end{matrix}$.

Case 2(*b*). One activator ion is compensated by two monovalent ions instead of by a vacancy, and the linear symmetrical position is the one of lowest energy, i.e. *CAC* along the [110] axis. An example of this class of phosphor is the MgO.Mn, Li phosphor recently described by Prener.[13] When excited by 3650 Å radiation at liquid-air temperature, it has a complex emission spectrum containing narrow bands which may be at least partly due to the vibrations of the centre.

Case 3. *A hexavalent ion.* (*a*) The centre consists of a linear arrangement of one activator ion and two lattice vacancies, i.e. *D A D* along the [110] axis. CaO.U is of this type, and it has been found to have a complex emission spectrum at liquid-air temperature when excited by 3650 Å radiation, Fig. 1(*a*). This sample was prepared from calcium carbonate and uranyl nitrate, and fired at 1250° C in air. The main unit which contributes to the vibrational fine structure is believed to be a UO_6 group, rather than a UO_2 group, and in this respect it is similar to the recently discovered uranates[14] which also have UO_6 groups. For comparison, the $Ba_2Ca\,UO_6$ spectrum, when excited by 3650 Å radiation at liquid-air temperature, is also shown, Fig. 1(*c*). Both spectra have a repetition frequency interval $\simeq 730\ cm^{-1}$, but the two spectra are relatively displaced.

Case 3(*b*). One hexavalent ion combines with four monovalent compensator ions to form a centre. There are two possible configurations which might occur, either a formation in which the monovalent ions form a square with the hexavalent ion at the centre, or a formation in which the monothough they are of comparable brightness at liquid-air temperature, and these two phosphors are considered strong evidence in favour of the localization of charge compensation.

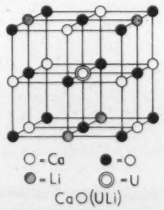


Fig. 2. The atomic configuration of CaO.U, Li

THE EMISSION SPECTRA OF SOME URANATE PHOSPHORS

In the course of an investigation of CaO.U it was found possible to make a uranate of composition Ca_3UO_6. It was shown[14] that the structure was similar to that of Ca_3WO_6 and, as expected from knowledge of the tungstates,[15] that it was possible to form a compound Ba_2CaUO_6 having a nearly cubic crystal structure. The idealized unit cell is shown in Fig. 3. Because of the greater simplicity in this structure, attention has been concentrated on these Ba_2CaUO_6 phosphors. Ba_2CaUO_6 is itself luminescent, see Fig. 1(*c*). The uranates can be activated by some of the rare earths, samarium and europium emitting their characteristic line spectra in the orange-red and red regions respectively; whereas

gadolinium, lanthanum and ytterbium act as intensifiers of the uranium emission. Of all these cases, the samarium

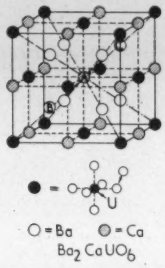


Fig. 3. The idealized unit cell of Ba_2CaUO_6

activation has been most studied. For Ba_2CaUO_6.Sm the configuration of lowest energy is probably obtained by replacing the Ba atoms B and C (Fig. 3) by Sm atoms, and

to interact with the electronic energy levels, causing further splitting of the spectral lines.

FLUORITE

Toorks[16] has claimed that CaF_2.U is intensified by the addition of CaO, and Kröger[17] has briefly discussed this result assuming charge compensation. Excluding the possibility of the entry of ions interstitially, there are still three possible methods of charge compensation. These are (*a*) compensation by lattice vacancies, (*b*) compensation by monovalent positive ions, and (*c*) compensation by divalent negative ions.

(*a*) The U ion replaces one Ca ion and is compensated by two lattice vacancies, i.e. *D A D*. This formation will be directed along the [110] axis, since the calcium ions form a face-centred cubic lattice.

(*b*) Four monovalent ions compensate one U ion, so that the positive ion configurations are exactly the same as for CaO.U, Li. Hence the stretched tetrahedral formation is the most likely configuration of lowest energy.

(*c*) Four oxygen ions replace four fluorine ions to compensate the excess charge, and Kröger[17] has stated that the U ion will be surrounded by four oxygen and four fluorine atoms. It is now suggested that these ions will be arranged

Fig. 4. (*a*) Ba_2CaUO_6 (1% Sm) (10 min); (*b*) Ba_2CaUO_6 (1% Sm, 1% Li) (20 min); (*c*) CaO (1% U, 0·2% Sm) (10 min)

removing the Ca atom at position A; whereas for the case of Sm, Li activation the Li and Sm ions probably occupy positions A and B respectively. However, an alternative possibility is that the Sm ions, and also the associated defects or monovalent ions, are all situated at Ca ion sites, the configurations being directed along the [110] axis. The emission spectra at liquid-air temperature when excited by 3650 Å radiation are shown in Fig. 4(*a*), (*b*). The energy transfer from the uranium ions is very good and no uranium emission is observable. The differences between the spectra are of the same type as those between CaO.U and CaO.U, Li, but are not so large, the line intensities still being markedly different, although the line positions are extremely similar. The emission spectrum of CaO.U, Sm is also included for comparison, Fig. 4(*c*), and it is obvious that the details of the emission spectrum of a rare earth ion can be greatly changed by the ionic surroundings.

It is known that the absorption and emission spectra of phosphors activated by rare earths contain too many lines to be explained on Bethe's theory of Stark splitting of the energy levels, when the rare earth ions are considered to be in positive ion sites, the neighbouring ions being normal. The present account explains the extra lines by the fact that each rare earth ion is in a field of much lower symmetry, due to the near proximity of a lattice defect or compensator ion. Furthermore, the vibrations of the centre may be expected

in a specific configuration, i.e. that the groups of oxygen and fluorine ions will each form a regular tetrahedron, as shown in Fig. 5. The spectra of CaF_2.U, CaF_2.U, O and CaF_2.U, Li, excited by 3650 Å radiation at liquid-air temperature are shown in Fig. 6. It is not claimed that the first and third of these phosphors are free from oxygen, as the uranium was introduced as a uranyl salt.

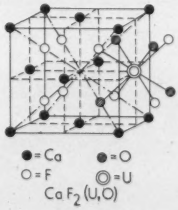


Fig. 5. The atomic configuration of CaF_2.U, O

There are also many interesting examples of fluoride phosphors activated by rare earths, and work is in progress on these phosphors. It will be interesting to note any systematic differences between the group of phosphors containing

vacancies and the groups containing different compensator ions.

It is also instructive to examine the implications of localized charge compensation in the general theories of sensitized luminescence and multiple band emission.

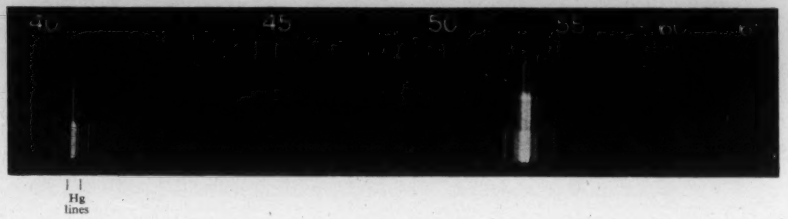


Fig. 6. (*a*) CaF_2 (0·1% U) (5 sec); (*b*) CaF_2 (0·1% U, 10% O) (5 sec); (*c*) CaF_2 (0·1% U, 1% Li) (30 min)

SENSITIZED LUMINESCENCE

In the many known cases of sensitized luminescence it is generally accepted that the sensitizer atoms absorb the incident radiation and then transfer the energy, directly or indirectly, to the activator ions which emit the fluorescent radiation. Botden[18] has recently summarized the existing theories in addition to presenting his own conclusions. He concluded that transport of energy from the sensitizer to the activator *via* the conduction band is very improbable because the quantum efficiency does not depend quadratically on the exciting radiation intensity. A similar objection holds for transport of vibration energy which could modify the activator potential energy curve in such a way that the activator could now be excited by another quantum of incident radiation. A more hopeful approach is that of supposing that direct transfer can take place from the sensitizer ions to the activator ions, or to other sensitizer ions, by a resonance process. Botden,[18] and Schulman and others[19] have performed calculations on the distance over which such transfer can take place, on the assumption of the random distribution of the sensitizer and activator ions. It is now suggested that this assumption is not valid and that the centres which have been already described will tend to pair. In this way, the present account is an extension of Kröger's[20] theory of associated-pairs and Murata and Smith's[21] idea of co-activators. It is to be noted, however, that it is centres and not ions which pair or tend to pair. For instance, a stable configuration can be obtained when a hexavalent centre in an oxide lattice is paired with one or two trivalent centres, i.e. $\begin{matrix} D\,A_6\,D \\ A_3D\,A_3 \end{matrix}$ or $\begin{matrix} D\,A_6D \\ A_3D\,A_3 \end{matrix}$. CaO.U, Sm is believed to be an example of this, Fig. 4(*c*), which would account for the remarkable energy transfer at liquid-air temperature. On the other hand, without localized charge compensation the U and Sm ions would have tended to repel each other. No strong evidence has been put forward against the formation of pairs, and certainly one cannot draw a clear conclusion from the fact that some sensitized phosphors have optical characteristics which are independent of the rate of cooling after firing,[18] as the configuration containing two or more centres may be formed and be reasonably stable even at the firing temperature. The mathematical analysis of the results is not unique and is in itself no proof of random distribution of the sensitizer and activator ions. The exact nature of the clusters is not always very clear as it will depend not only on the charge of the ions, but also on the size and on the magnetic and other properties of the ions. However, the coulomb forces can often be expected to be predominant, e.g. in NaCl.Pb, Mn or KCl.Pb, Mn the Pb and Mn centres will tend to pair with each other and amongst themselves, i.e. $\begin{matrix} D\,\mathrm{Pb} \\ \mathrm{Mn}\,D \end{matrix}$ or $\begin{matrix} D\,\mathrm{Pb} \\ \mathrm{Pb}\,D \end{matrix}$ or $\begin{matrix} D\,\mathrm{Mn} \\ \mathrm{Mn}\,D \end{matrix}$, and clusters of the first type will be responsible for the sensitization.

A great advantage of this theory of specific configuration is that it is not necessary to postulate long range resonance processes between unlike ions. It is still expected that resonance transfer between like atoms can take place over considerable distances of the order of 50 Å, and this is reasonable on Förster's[22] theory of resonance transfer between equivalent molecules. Dexter[23] has extended this theory to include the forbidden transitions occurring in the luminescence of inorganic materials.

THE THEORY OF MULTIPLE-BAND EMISSION

In a similar way, the theory of localized charge compensation tends to support the cluster theory of multiple-band emission. When the ion has a different co-ordination number (C.N.) in different substances there may be a change in the colour of the emission, e.g. $CdWO_4$.U is red, C.N. = 4; Ca_2MgWO_6.U is green, C.N. = 6. In a specific crystal structure, however, it would appear that clustering is the most likely mechanism by which changes in the environment of the activator ion may occur. For instance, trivalent, tetravalent and hexavalent ions in a face-centred cubic oxide crystal, will tend to pair when electrical neutrality is achieved by the presence of defects. Trivalent and tetravalent ions will tend to pair when compensated by monovalent ions.

There may even be a tendency for the hexavalent ions, when compensated by monovalent ions, to pair; but this is expected to be very slight, owing to the screening of the hexavalent ion by the symmetrically arranged monovalent ions. Even when no charge compensation is necessary, there will still be ionic properties which will tend to reduce the randomness of the distribution of the activator. There will be least disturbance of randomness in the case of an activator ion where no charge compensation is necessary, and where the electronic configuration in the ground state consists of complete shells or sub-shells of electrons. An example of this is KCl.Tl, and the Tl^+ ions are believed to be nearly randomly distributed in K^+ sites. A detailed X-ray investigation of the KCl.Tl system, carried out by Runciman and Steward,[24] showed that the Tl^+ ions substituted for

K^+ ions. Both the line positions and intensities were in agreement with the values predicted from a random distribution of Tl^+ ions.

Where the sub-shell is incomplete as in Mn^{2+}, then there is likely to be a strong deviation from randomness, and Larach and Turkevich[25] have obtained results which may be interpreted in this way.

Evidence was presented earlier to show that the centres in CaO.Bi cause a new band to appear when pairing occurs, in a similar fashion to the emission bands at 3755 and 5800 Å due to Tl^+ ion pairs in KCl[26]. Pb^{2+} ion pairs in CaO also are the likely cause of the red emission band in the CaO.Pb phosphor, and this similarity is not surprising, since Bi^{3+}, Pb^{2+} and Tl^+ are all iso-electronic with the neutral Hg atom. Some weak vibrational lines have been found superimposed on the red emission band of CaO.Pb, when excited by 3650 Å radiation at liquid-air temperatures, and these are of a very similar type to those reported by Randall[27] for CaO.Mn. They occur at approximately 6060, 6150, 6230, 6300 and 6360 Å.

CONCLUSION

It has been shown that a theory of localized charge compensation provides a framework capable of synthesizing many of the previously puzzling results in the luminescence of ionic crystals. In consequence of this theory calculations which have been based on the assumption of a random distribution of activator ions, must be considered as requiring revision in many cases. It will be possible to calculate the binding energies of the centres, the absorption and emission of phosphors, etc., on the new theory using the established methods of solid-state physics. However, when a detailed knowledge of the vibrations of the ions in the centre is required, these calculations will be rather formidable, owing to possible anharmonicity of the vibrations.

The spectra of CaO.U, Li, CaO.U, Sm and of various uranate phosphors have been described, and it appears that alkaline earth oxide, uranate and fluoride phosphors form an ideal system for the study of the effects caused by changes in the surroundings of the luminescent ions. It is fortunate that both the uranium and the rare earth emission spectra consist of lines and narrow bands, enabling a detailed analysis to be made of the effects of slight changes in the luminescent centres.

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DISCUSSION

Dr. P. Brauer: I am impressed by Mr. Runciman's success in calculating the ratio of the vibration frequencies for CaO.Bi, for we tried in vain to calculate similar vibration frequencies, found by Tomaschek for Sm^{3+} and Pr^{3+} in alkaline earth oxides and sulphides. We did not know how to calculate the reduced mass of the vibrating system.

When an activator ion of different valency or charge is introduced into an ionic lattice, the valency of the activator may have other values than those in ordinary chemical compounds. For Tl and the alkaline halides it is probable that Tl is monovalent. Nevertheless we did not consider it correct to exclude other possibilities and therefore used the complete Mott–Littleton theory[1] to estimate how many foreign ions will enter the lattice at a given temperature and a given concentration of these ions in another phase; and, in addition, to explain the very great differences in the preference of a foreign ion for different host lattices.[2]

The charge of the foreign ion may be completely uncertain. For Eu in the alkaline earth oxides and sulphides we have shown by calculation that it has to be trivalent in the oxides but divalent in the sulphides, selenides and tellurides, when the pressure of the gaseous phase during preparation is considerable. Thus we explained the different emission spectra of the phosphors.[3] However, the valency of Eu may change if the pressure of the gaseous phase is changed. Thus mixed crystals of SrO and EuO (divalent Eu) were made using reducing conditions,[4] in spite of the fact that pure EuO is unknown. This agrees with our calculation, according to which the chemical affinity of the reaction

$$\underset{\text{(in SrO)}}{2Eu^{3+} + |Sr^{2+}|} + SrO \rightleftharpoons \underset{\text{(in SrO)}}{2Eu^{2+}} + \tfrac{1}{2}O_2,$$

where $|Sr^{2+}|$ is a Sr^{2+} vacancy in the lattice, is at least 3 eV greater than the affinity of

$$Eu_2O_3 \rightleftharpoons 2EuO + \tfrac{1}{2}O_2$$

In this manner it is possible to prepare quite different samples of SrO.Eu: white ones containing Eu^{3+}, charge compensated probably by Schottky holes, and pink to deep violet ones, containing Eu^{2+} without charge compensation.

Charge compensation should, therefore, be discussed only in connexion with changes of charge, and we must calculate the free energy or the affinity of the chemical reaction as a whole.

Dr. F. A. Kröger: When ions of opposite effective charge are present in a solid, energy conditions favour a clustering into pairs or even larger agglomerations while entropy conditions tend to keep them apart. At the high temperature of preparation a fraction of the ions is present in the "associated" form and another fraction in the "dissociated" form. During cooling association is favoured, but below a critical temperature for ionic migration, further association is impossible.

In general both "free" ions and associated pairs may be responsible for luminescence, trapping, etc., and, as has been shown for ZnS.Ag^+, Pr^{3+}, it is probable that while the blue luminescence originates in Ag^+ at sites far from Pr^{3+}, characteristic Pr^{3+} emission originates both from Pr^{3+} ions and from Ag^+–Pr^{3+} pairs. I do not agree with Mr. Runciman's preference for the pairs.

(*b*) It is stated that the position of spectral lines is independent of the symmetry and the strength of the electric field in which the activator atom is situated, but that the intensity of the lines is dependent on them. This seems to be in conflict with Bethe's theory.[5]

Runciman mentions that often oxides or sulphides activated by rare earth ions do not show the simple fluorescence pattern predicted by the Bethe theory for cubic lattices. Deutschbein[6] and Brauer[7] have shown, however, that MgO, CaO, SrO and BaO activated by Eu^{3+} emit a strong line in the red predicted by the Bethe theory for pure cubic symmetry, all other lines present being at least ten times weaker.

(*c*) The proposed return to the pair theory of sensitization which I once advocated is impossible, for Botden[8] has proved that this theory cannot explain, in particular, the increase of the ratio of manganese to sensitizer emission with increasing concentration of sensitizer.

The centres proposed by Runciman may well exist, but in general they do not play the predominant role he assigns to them.

Dr. F. E. Williams: I support the remarks of Dr. Brauer and of Dr. Kröger regarding the importance of the entropy, in addition to the potential energy, in determining the relative concentration of the associated and unassociated centres.

The emission spectrum of CaO.Bi, Li can be adequately accounted for on the basis of isolated Bi^{3+} at cation sites. Bi^{3+} is isoelectronic with Tl^+ and would be expected to exhibit similar luminescence properties. The two emission bands can be attributed to the $^3P_1^0 \rightarrow {}^1S_0$ and the $^1P_1^0 \rightarrow {}^1S_0$ transitions; the fine structure, to the vibrational levels of the activator system consisting of Bi^{3+} and its six nearest neighbour O^{2-} ions. From the coulomb interaction alone the force constant K for the activator system of CaO.Bi should be six times that for KCl.Tl. The effective mass M should be approximately one-half. Since the separation ΔE of the vibrational levels is $\hbar\sqrt{(K/M)}$ an emission fine structure separation of 0·05 eV is calculated, in good agreement with the experimental value of 0·06 eV.

Dr. B. V. Thosar: While considering the atomic configurations of luminescence centres it would be of interest to examine the structure of luminescence in the deep red due to Cr^{3+}, in relation to the crystal structure of the various natural oxides and silicates in which it becomes luminescent by replacing the Al^{3+} ion. From Deutschbein's results the following conclusions may be drawn:

(*a*) The red luminescence, normally a doublet, is characteristic of a Cr^{3+} ion at the centre of an octahedron, the corners of which are occupied by six oxygen ions or other anions.

(*b*) This octahedron shares corners, edges or faces with other polyhedra and may become distorted. The amount of this distortion can be correlated with the separation of the two lines of the doublet. In MgO, a regular cubic crystal, there is a single line emitted instead of a doublet.

(*c*) The case of disthene, Al_2SiO_5, is of special interest. In this, octahedra with Al at the centre and O at the corners form chains along the *c*-axis by sharing edges. Similar octahedra, structurally non-equivalent with the former, occur in the crystal and link the chains laterally. Cr^{3+} replacing Al^{3+} ions at the centre of these two different kinds of octahedra should give luminescence lines not identical in wavelength, and this is indeed the case. There are in disthene two emission doublets and not one.

Mr. J. Ewles: The suggestion that the vibrational frequencies which I reported in the resolved CaO.Bi spectrum are attributable to two modes of vibration of a linear quadrupole is ingenious but can hardly be sustained in its present form.

(*a*) The ratio $\sqrt{3} : 1$ of the two vibration frequencies, deduced from the model, does not hold for SrO.Bi (2·05), CaS.Bi (1·93), MgO.Bi (2·21) and CaO.Pb (1·92).

(*b*) The two frequencies involved in the electron vibration band formula must refer to the vibration frequencies of the luminescence centre in the upper and lower states, and not to two different lower state frequencies.

(*c*) It is tempting to accept the charge compensation idea to explain the effect of a flux, but the addition to a divalent host lattice of a flux containing a monovalent ion (e.g. CaO.Bi, NaCl) does not alter the luminescence spectrum as would be expected if the monovalent ion forms part of the centre, unless it is assumed that an ineradicable trace of flux is always present in the purest ionic crystal. It is certainly true that luminescence effects can be produced by a concentration of 10^{-7} of activator.

Author's reply: Dr. Brauer has shown how the charge on an impurity ion may vary with the conditions of preparation. In the cases I have considered the ionic charge is fairly certain and it is possible to consider how charge compensation may take place without considering all the chemical reactions involved.

Dr. Kröger has clearly indicated the importance of entropy in considering the degree of clustering which takes place. Experimental results to date indicate that there is a preference for clustering in many cases, but further experimental and theoretical work should clarify this point. I have nowhere made the statement given in Dr. Kröger's point (*b*), but have quoted the spectra of CaO.U, Sm and Ba_2CaUO_6.Sm to prove the contrary. However, the changes in the field caused by differences between the nearest positive ions in Ba_2CaUO_6.Sm and Ba_2CaUO_6.Sm, Li produce only slight modifications in the line positions. This seems reasonable as the nearest negative ions make the largest contributions to the field.

Kröger's point (*c*) is also not valid, since I do not make the assumption, involved in Botden's deduction, that only absorption in a sensitizer ion adjacent to an activator ion will give rise to activator fluorescence. On the contrary I have stated that it is still expected that resonance transfer

between like atoms can take place over considerable distances. Transfer between unlike ions over large distances is not considered necessary to explain the experimental results and in this respect I disagree with Botden's conclusions, which were based on a random distribution of both activator and sensitizer ions.

I now agree with Dr. Williams that the fine structure in the CaO.Bi spectrum can be attributed to vibrations of the six oxygen ions surrounding the Bi^{3+} activator ions. The Bi^{3+} ions need not be isolated, and the difference in relative intensities of the red and blue bands for CaO.Bi and CaO.Bi, Li can be satisfactorily ascribed to the association of the positive ions. The spectrum seems too complex for all the lines to be due to radial symmetric oscillations of the oxygen ions. The change in charge distribution when the Bi^{3+} ion goes from a dumb-bell 6p state oriented along the [110] axis to a spherical 6S state will cause the oxygen ions to rearrange their equilibrium positions in a way which can be described by three independent parameters. Hence we may expect three normal modes of vibration rather similar to the three Raman vibrations of an octahedral molecule such as SF_6. The transition is similar to that of Tl^+ in the KCl.Tl phosphor,[9] and the existence of three degrees of freedom demonstrates the limitations of the configuration co-ordinate model used by Williams. This new model may explain some extra lines recently observed in both the absorption and emission spectra of a CaO.Bi phosphor at liquid nitrogen temperature: these lines were not easily explicable in terms of the previous model. Yet the objections raised by Mr. Ewles are not conclusive and I still maintain that the two vibrational frequencies observable in the fluorescence spectrum refer to the ground state. This necessitates a modification of the vibration formula used by Ewles to represent the line positions. The absorption spectrum is almost a "mirror image" of the fluorescence spectrum, but the vibrational frequencies are considerably smaller. Useful confirmation comes from the results of Ewles and Lee[10] which show that both sets of lines in the emission spectrum still exist at 20° K; at this temperature with a Boltzmann distribution almost all the excited ions should reach the lowest vibrational state before emission takes place.

There is definite evidence that the addition of Li_2CO_3 to the CaO.Bi phosphor before firing alters the emission spectrum as described above. Compensation by monovalent ions will not take place if it is energetically unfavourable, e.g. because of an unsuitable ionic radius, and it may not be possible for the Na^+ ions to enter the CaO lattice in the case quoted by Ewles, where only a normal flux action appears to occur.

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Paper 16

Absorption, emission and storage of energy in phosphors

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The characteristics of photoconducting phosphors of the sulphide class are reviewed in relation to the accepted energy band model for such phosphors. It is shown that the model is inadequate to explain the processes involved in the thermal and optical ejection of trapped electrons. Considerable evidence points to the coexistence of emission, trapping and "killer" systems in large centre complexes. Preliminary results of studies on single crystal specimens show that the dielectric changes shown by microcrystalline phosphors on excitation are associated with grain boundary effects rather than with trapping effects in the crystal volume. Loss changes in single crystals agree with photocurrent values in d.c. fields. Preliminary measurements of long wavelength absorption bands associated with trapped electrons in excited cadmium sulphide crystals are reported.

In recent years the energy band model for crystalline solids has been extensively applied to the explanation of the characteristics of photoconducting phosphors. There is information of several kinds on these phosphors which is still not satisfactorily interpreted on such a theoretical basis. However, most of the past experiments have been made on microcrystalline powders and therefore such effects as photoconductivity and dielectric changes are not easily measured in a quantitative way. In recent years the development of preparative methods for single macrocrystals of cadmium and zinc sulphides has provided opportunities for a more detailed study of such phenomena in relation to luminescence. Some of the preliminary results for single crystal specimens are discussed in this paper, which also attempts to review the data for conventional phosphors and to discuss it in relation to the energy-band model. For these purposes use will be made of Fig. 1 which gives a schematic diagram of the energy band system usually accepted for sulphide phosphors. The diagram includes the most probable optical and thermal transitions for electrons. For simplicity, only single levels are inserted for emission centre and trapping states. Fig. 2 is a schematic diagram which represents the usual forms of the absorption, excitation, emission and trapped electron ejection spectra together with the spectral response of photoconductivity and the variation of trap filling efficiency with wavelength of the exciting radiation.

ABSORPTION, EXCITATION AND EMISSION PROCESSES

The usual absorption spectrum of a sulphide phosphor is given in Fig. 2(*a*). The lattice absorption is represented by transition *A* of Fig. 1. The excitation resulting from this absorption is confined to the crystal surface because of the high absorption coefficient and is thus of relatively high density. It gives rise to high local concentrations of free electrons and positive holes, but a high rate of recombination of the latter is probable, the process being non-radiative at

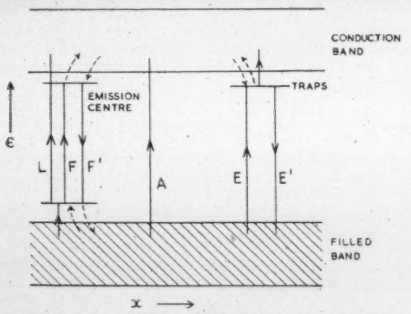


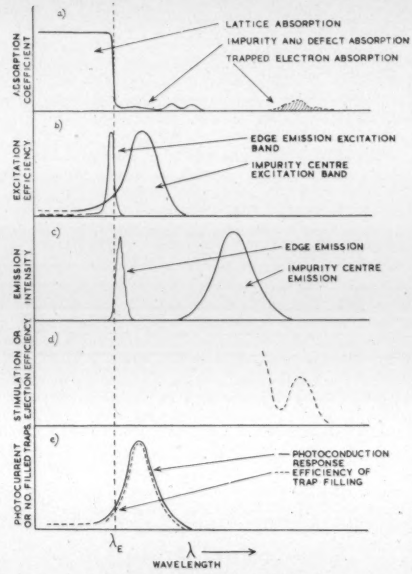
Fig. 1. Energy band scheme for photoconducting phosphor

normal temperatures. Photoconduction response is of low efficiency in this excitation region, probably due to the recombination rate which will adversely affect the life time of free carriers.

At low temperatures lattice absorption results in an "edge" emission in phosphors such as ZnS, CdS, ZnO, CaO, etc., when these are unactivated or have very low impurity activator concentrations. As shown by its excitation spectrum in Fig. 2(*b*), the emission is most efficiently excited by wavelengths near the absorption edge. It occurs immediately outside the absorption edge, is relatively sharp compared with impurity activator emission bands, and has a sub-band structure with frequency differences for these bands which correspond approximately to the Reststrahlen frequency of the respective lattice.[1] In this laboratory the excitation and emission spectra have been measured for the "edge" effect in cadmium selenide. The spectra show the same general characteristics as in the case of cadmium sulphide.[1]

Schön[2] has suggested that the edge emission is due to the recombination of trapped electrons and positive holes, the latter being captured first in the coulomb field of the electron. The transition *E'* of Fig. 1 represents this edge emission. Kudryavtseva[3] attributes the edge emission to a "lattice resonance" effect. Little is known experimentally of the edge emission with regard to its temperature dependence and its phosphorescence characteristics. The excitation spectra measured in this laboratory for sulphides and selenides peak sharply near the absorption edge and indicate the possibility that the absorption and emission are characteristic of specific sites in the lattice, such as those forming the trapping states. Kröger and Hellingman[4] have shown that the edge emission decreases in intensity as activator impurity and compensator ions are introduced into the lattice. Their results are relatively quantitative but give little information about the emitting centres responsible. Stöckmann[5] has made a theoretical study of the relative probabilities of radiative and non-radiative transitions in the trap systems, but no experimental values for the quantities involved are available.

The most interesting part of the absorption spectrum of sulphide phosphors is the "tail" of the absorption spectrum lying outside the absorption edge of the matrix lattice. This may be structureless, but often the activating impurity gives rise to some structure in this tail.[1] In Fig. 1 both transitions *L* and *E* correspond to this absorption region. In the case of



λ_E is the wavelength of absorption edge.

Fig. 2. Schematic diagram of absorption, excitation, emission and trapped electron ejection spectra of a sulphide phosphor, together with the spectral response of photoconductivity and the variation of trap filling efficiency with wavelength of the exciting radiation

ZnS.Mn phosphors the transition *F* also occurs, the absorption and emission processes being confined to the emitting centres, and photoconductivity and trap filling being absent.[6] If processes *L* and *E* occur then both free electrons and free positive holes should be created. However, the following experimental evidence appears to eliminate the possibility of the transition *E*:

(*a*) The luminescence excitation spectrum for the impurity centres reaches its maximum in this tail region of the absorption spectrum, see Fig. 2(*b*), and in many cases quantum equivalence obtains at the maximum. If positive holes were made mobile by absorption in the tail region then their recombination with trapped electrons would give a lower efficiency than that for quantum equivalence.

(*b*) Variations of photoconduction and number of trapped electrons with wavelength show maxima in the same region as the luminescence excitation spectrum, the conductivity often reaching quantum equivalence at the maximum. The

existence of free, positive holes would detract from the efficiencies of both these processes.

With respect to the impurity activator centres such as Cu, Ag, Au, etc., in zinc sulphide, Klasens[7] has suggested that the ground state of the centre is a lattice energy state perturbed by the presence of the cation. This seems an attractive hypothesis. Coupled with the assumption of an extensive excited state for such centres it supports the conclusions of other workers that the activator centre is a large complex which involves many atoms of the matrix lattice, and as suggested later in this paper, which contains at least some of the states responsible for electron trapping. It is of interest here to note that the further the excitation spectrum is from the absorption edge (towards longer wavelengths) the further the emission spectrum moves in the same direction. The two phosphors ZnS.Zn and ZnS.Sn may be compared for this purpose.[8] The relative positions of the excitation and emission bands and the lattice absorption edge demand the insertion of an excited state into the level scheme of Fig. 1 for the emission centres. This excited state is often omitted in the models adopted by other workers, for example see ref. (9). If this state is included then the probability of loss of electrons from excited centres by thermal or optical activation into the conduction band must be allowed.

Excitation of sulphide phosphors leads to the appearance of new absorption bands at longer wavelengths. These have been observed in powder form materials by several workers, for example, by Urbach and others,[10] and for zinc sulphides by Hoch.[11] Using a double-beam spectrophotometer system developed in this laboratory by D. E. Mason,* A. Halperin† has succeeded in measuring these bands for an excited cadmium sulphide crystal 1 mm thick, both at room temperature and at liquid air temperature. The crystal shows absorption with sub-bands overlapping each other and having a main peak at 7400 Å, i.e. at the emission maximum for CdS.Ag phosphors. However, this specimen was unactivated. The absorption is characteristic of trapped electrons and the bands are bleached by radiation lying within them. Quantitative studies of dependence on excitation wavelength, temperature and crystal constitution are proceeding. It is interesting to note that in the measurements at 90° K the absorption at the maximum was 8% of the incident radiation, corresponding to a coefficient of 1 mm^{-1}.

ENERGY STORAGE PROCESSES IN PHOSPHORS

The usual methods of studying the storage of energy in phosphors are by thermal and optical ejection measurements on trapped electrons. However, the use of the thermal glow experiment as an indicator of the distribution of trapping states in a phosphor is now open to question. Schön[12] has pointed out that the thermal activation of positive holes from empty emission centres into the filled band at a sufficiently high temperature, and their recombination with trapped electrons, will result in the loss of the latter to the "glow curve" process. Evidence of this effect is available from the recent experiments of Hoogenstraaten,[13] and from experiments made in this laboratory using special combinations of optical and thermal stimulation of phosphors.[14,15] The latter experiments have revealed the existence of large numbers of trapped electrons in sulphide phosphors which never take part in the thermal glow process or in phosphorescence. A method has been developed for reconstructing the "non-radiative portion" of the "glow" curve.[15]

From the available evidence we may summarize the characteristics of trapping effects as follows:

(*a*) Thermal activation of trapped electrons is not followed by appreciable retrapping of the electrons, even under the most favourable conditions.[16]

(*b*) Optical ejection of trapped electrons does result in a high degree of retrapping with revelation of large numbers of trapped electrons which never play a part in the thermal glow process.[14,15]

(*c*) No simple relation exists between the trap distribution measured thermally and that measured optically (stimulation spectrum).

(*d*) Optical ejection spectra, Fig. 2(*d*), usually consist of a broad band overlapping the emission spectrum (cf. absorption bands due to excitation in CdS) with subsidiary band(s) at longer wavelength. These bands at longer wavelengths are sharper in form than the *F* centre bands in KCl and so arise from a very specific kind of absorption site in the phosphor.[14]

(*e*) For a given temperature of excitation there exists a lower temperature below which optical ejection of electrons by a given monochromatic irradiation does not occur. The temperature is lower the shorter the wavelength of the radiation. Detailed evidence suggests that ejection is in two stages, optical absorption being followed by thermal activation, a similar process to that for optical bleaching of *F* centres.

(*f*) During the thermal glow experiment on single crystals of ZnS and CdS a conduction current occurs in the presence of an applied field. The analysis of this "glow" current in relation to the glow curve is complex but preliminary results obtained in this laboratory[17] appear to confirm the absence of retrapping during thermal activation processes.

(*g*) In contrast to microcrystalline powders,[18] single crystals of zinc and cadmium sulphides do not show large changes of dielectric constant when excited.[19] Loss changes do, however, occur, but these can be correlated with the photoconduction in d.c. fields. No relaxation effect is found for such crystals in the usual frequency range (1–10 Mc/s) where the effect is found in powder-type phosphors. As suggested by Dropkin and Kiszenick,[20] the dielectric constant changes in powder phosphors can be explained as largely due to grain boundary dipole layers.

(*h*) Single crystals of ZnS and CdS show semiconduction if their temperature is raised sufficiently. So far experiments indicate that they behave as *n*-type semiconductors.

The absence of retrapping during thermal ejection of trapped electrons suggests that some of the traps are contained in the complex activator centres and that such ejected electrons do not pass through the conduction levels to reach the excited state of the centre. Detailed investigations of the "current glow curve," particularly in relation to the thermoluminescence curve under various conditions, may help considerably in distinguishing the exact process of thermal ejection as compared with optical ejection of trapped electrons. It is worth noting that studies of the thermal bleaching of *F* centres in the alkali halides lead to the conclusion that the ejected electrons do not reach the conduction band before returning to their ground state.[21]

Some light has been thrown on the nature of trapping states in zinc sulphide by Hoogenstraaten[13] and by Hoogenstraaten and Klasens.[22] They associate the traps with the compensator ions such as Cl^-, Br^-, Ga^{+++}, Al^{+++} and Sc^{+++}, or in other cases with the presence of oxygen or cobalt. However, their experiments do not indicate whether these ions produce traps in association with the activator centres, and so cannot decide the validity of the assumption that traps occur within a large centre complex. Some experi-

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ments on ZnS.Cu phosphors by Gibson,[23] in which he studied the glow curves and luminescence efficiency for different activator concentrations, showed that increasing activator density perturbs first the trapping states and then the emission efficiency. From simple considerations this supports the complex centre hypothesis. Other evidence from experiments on fluorescence quenching by nickel in ZnS.Ag also indicates association between activator and "killer" ions.[24]

CONCLUSION

It is evident from the above discussions that the energy-band model of Fig. 1 is too simple to accommodate the complex processes indicated by optical ejection experiments, and by experiments which indicate the existence of an extensive centre complex in which emission and trapping may occur. Overlap of ejection and emission spectra also introduces a complication in analysis of phosphorescence or thermal glow curves, since the emitting phosphor "self" stimulates or quenches. This process is not negligible under normal emission intensities.

It would be useful to have independent evidence of positive-hole motion between centres and traps, as postulated by some workers[9] to explain temperature quenching of fluorescence. Some attempts might be made to inject positive holes into single crystals during luminescence excitation at temperatures below those for temperature quenching by application of a suitable electrode system to the crystal. For cadmium sulphide the electrode work function to do this would have to be rather large ($\simeq$6eV) compared with that of electrodes for ohmic contacts on the crystal ($\simeq$4 eV). Such injection would also provide valuable indication of the possibility of positive hole-electron recombination in trapping sites.

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DISCUSSION

Dr. D. Curie: Many experiments seem to show that in zinc sulphide the deep traps are due to the activator impurity, and possibly situated in the vicinity of centres. But the traps whose depth is near 0·3 eV seem to exist in the sulphide before the introduction of centres. Garlick has shown that the "blue" part of the thermoluminescence curve depends on the lattice structure (blende or wurtzite) and is approximately the same for activators Zn, Ag or Cu.[1] In CaS.Bi, on the contrary, the deep traps seem to be in the lattice, the others near the bismuth.[2]

The Bohr model of traps is meaningless for traps in the activator complex, but it may apply to traps in the lattice. The formula

$$E = R/K^2, \text{ where } R = 13{\cdot}5 \text{ eV}$$

is not valid, because the lattice field is changed by the polarization due to the trapped electron.

However, if

$$\frac{1}{K_e} = \frac{1}{K_0} - \frac{11}{16}\left(\frac{1}{K_0} - \frac{1}{K}\right)$$

where K_0, K and K_e are respectively the high frequency, static, and "effective" dielectric constant, the thermal activation energy is then

$$E = R/K_e^2$$

and the optical ionization energy is[3]

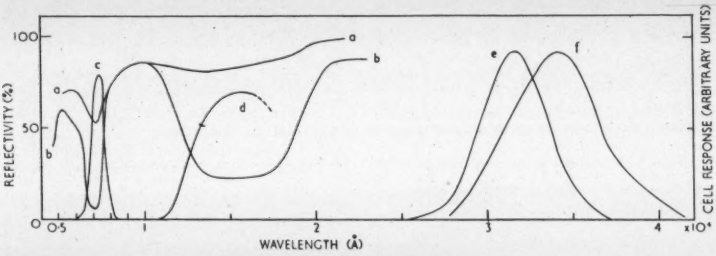
$$h\nu = R/K_eK_0$$

For zinc sulphide (blende), $K_0 = 5{\cdot}07$, $K = 8{\cdot}3$, and the calculated value of $E = 0{\cdot}3$ eV agrees well with the thermoluminescence peak at $T = 150°$ K if $E = T/500$.

Dr. M. J. Dumbleton: Cobalt as an activator in zinc sulphide gives rise to an emission band in the infra-red region, with a maximum at 3·2 μ at room temperature (see Curve *e* of the figure). The efficiency of the phosphor increases with firing temperature, at least up to 1200° C, and the optimum activator concentration is 10^{-3} parts Co by weight. The infra-red band persists in the presence of 10^{-4} Cu, and both the usual emission due to copper and that due to cobalt can be observed in the same phosphor, although the copper emission is killed if more than 10^{-4} Co is present. The cobalt gives rise to two absorption bands, a narrow one at 7000 Å[4] and a broad one extending between 11 000 and 20 000 Å (Curves *a* and *b*). Similar bands, shifted about 1000 Å to shorter wavelength, were found in the absorption due to cobalt in a flattened borax bead. Here the absorption is due to the Co^{2+} ion[5]. The excitation spectrum for the cobalt emission is shown in Curve *cd*. It has a narrow and a broad band coinciding exactly with the two bands in the absorption spectrum. It seems clear that we are dealing with a transition within the cobalt ion, although some perturbation of the levels by the surrounding lattice is possible, as is shown by a small spectral shift (accompanied by a marked decrease in efficiency) on adding CdS (Curve *f* for 60% CdS). Other

examples of new infra-red emitting phosphors of the sulphide group are described elsewhere.[6]

Dr. F. A. Kröger: Although Dr. Garlick presents a complete level scheme for ZnS type phosphors, he assumes that optically only the transitions leading to the formation of free electrons appear. There is no fundamental reason for this, and I believe that essentially all transitions may take place.



a, b: reflexion spectra of ZnS.Cu, Co (10^{-4} Cu); *a*, 10^{-5} Co; *b*, 10^{-3} Co.
c, d: excitation spectrum of ZnS.10^{-3} Co (response of total emission to exciting light from a tungsten lamp through monochromator with LiF prisms); band *c* drawn on 30 times the vertical scale of band *d*.
e: emission spectrum of ZnS.10^{-3} Co (as for response of PbTe cell, with LiF prisms).
f: emission spectrum of 40% ZnS.60% CdS . 10^{-3} Co.

The main argument against the occurrence of excitation from the valency band to empty trapping levels is the quantum efficiency of unity claimed for the excitation of normal luminescence. This figure may be doubted, for Antonov-Romanovsky and Epstein[7] as well as Botden (unpublished) never found efficiencies markedly exceeding 0·5 even at the maximum of the excitation spectrum. Garlick ascribes infra-red absorption caused by excitation to the emptying of traps. The other possibility, the liberation of holes, may also occur, and there are indications that both processes happen together. When electrons are liberated, normal fluorescence follows (infra-red stimulation); when the holes are liberated, the fluorescence is either quenched (ZnS.Cu, Co) or another emission follows (ZnS.Cu, Pb).[8] The liberation of holes by infra-red stimulation is also found in CdS, where infra-red radiation decreases the concentrations of current carriers in a photoconducting crystal: this could never be explained by the liberation of electrons into the conduction band.

Dr. W. Hoogenstraaten: Dr. Garlick assumes the existence of a complex centre, containing traps associated with the activator, from the following facts:

(*a*) There is no retrapping of electrons, thermally activated from traps. The glow curves after full and weak excitation published as evidence for the absence of retrapping[9] show, however, an appreciable relative decrease of the low temperature glow for the weakly excited phosphor. That this effect is not much stronger, as one might expect if the capture cross-sections for traps and centres were of equal order of magnitude, may be explained by the presence of very deep traps. Such traps will be invisible in the glow curve because of temperature quenching,[10] but they may retrap a considerable portion of the electrons from the deepest "visible" traps during the glow of the weakly excited phosphor. More direct evidence for retrapping of thermally activated electrons is provided by the electro-stimulation experiments (Gudden–Pohl effect) of Mattler and Curie,[11] who showed that certain groups of traps, exhausted by the application of an alternating electric field, are gradually refilled from deeper unaffected traps. Further, the absence of retrapping of thermally activated electrons should (as Garlick points out) imply that such electrons do not pass through the conduction band to reach the excited centres. This conflicts with the experiments which show conduction (or dielectric changes) in single crystals (or powders) of zinc sulphide during thermal glow. As optical ejection of electrons from traps into the conduction band does result in retrapping of these electrons, there is no reason to assume that this could not happen to electrons liberated by thermal activation and also reaching the conduction levels.

(*b*) The association between activators and traps is also deduced from experiments on ZnS.Cu with increasing copper content.[12] Here the high temperature glow peak disappears, and at still higher concentrations the fluorescence is quenched. This is no proof that the deeper traps and the Cu activators are closely connected, for it can be simply explained by concentration quenching by excess copper, in which the phosphorescence and glow are affected at smaller killer concentrations than the fluorescence. Thus the disappearance of the high temperature part of the glow curve is not caused by destruction of the deeper traps. A strong argument against a general association between activators and traps, caused by halogen or trivalent metal ions (coactivators), is the mutual independence of the emission spectrum of an activator and the trap depth of a coactivator.[13,14]

Author's reply: With reference to the discussion by Dr. Curie, his conclusions from glow curve data in his reference (1) may be doubtful as in these phosphors we made no attempt to exclude oxygen during firing.

As regards the question of hole migration raised by Dr. Kröger, it is of course essential to the Klasens–Wise theory of thermal quenching and for later conclusions of his co-workers regarding ZnS.Cu, Co and ZnS.Cu, Ni. However, no direct evidence of hole motion has yet been obtained. As indicated in my paper (reference 24) semiconduction during thermal quenching is predominantly *n*- not *p*-type. It is of interest to note that Broser and Broser–Warminsky find it necessary to assume very small hole mobility in ZnS and CdS to explain their results.

With respect to retrapping, the conditions in the experiment quoted[9] are exceedingly favourable to retrapping. If in addition there are empty deep traps stable beyond the glow curve limit as suggested by Dr. Hoogenstraaten, then this increases the ratio of empty traps to empty centres ($\sim$10 000 : 1). Yet, in spite of this, emission still occurs in the first glow peak with a light sum of the order expected

from the energy of the feeble excitation pulse. However, for the phosphor used there were no serious discrepancies between build-up and glow light sums, which would reveal the deep traps. It is obviously necessary to examine the retrapping problem more carefully for the case of thermal activation. The experiments of Mattler and Curie,[11] for example, could be developed to give a more conclusive answer by using glow curves after electrical exhaustion of traps. I agree with Hoogenstraaten that if thermally excited electrons reach the conduction levels they should be retrapped but data on conduction during glow are not conclusive, since this can arise from displacement currents as the traps empty into centres or, in powders, from dissipation of an intergranular space charge.

The question of association of emission centres and traps might be clarified by paramagnetic resonance experiments.

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Paper 17

Luminescence and electrical conductivity of crystal phosphors

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Using a general form of the energy band model for a crystal with a wide distribution of lattice defect levels, comprehensive equations are developed which relate the luminescence and photoconduction in crystal phosphors to excitation intensity, time and temperature for different physical conditions. These include steady state excitation, phosphorescence, photoconduction decay and continuous warming of the phosphor. Measurements on single crystals of ZnS and CdS show good agreement between the theory and experiment.

INTRODUCTION

Crystalline phosphors often show photoconductivity as well as luminescence on excitation. This experimental fact, discovered many years ago,[1] forms the basis of theoretical considerations using the energy band model for metals and semiconductors.[2,3] As long as crystal phosphors were available only in powder form, photoconductivity measurements were difficult because of grain boundary resistance and so, with a few exceptions,[4] only the luminescence characteristics were interpreted.

Since the development of single crystal phosphors,[5] the number of publications on their photoconductivity has greatly increased[6–12] and so the optical and electrical characteristics of these phosphors are better known. In recent years important progress has been made and there now exist several theoretical treatments by which experimental observations can be interpreted.[13–16] The following approach provides a generalized form by which the conductivity and luminescence measurements can be related to the energy states of a crystal lattice perturbed by impurities or defects, and to the electronic transition probabilities between these various states.

THE BASIC EQUATIONS

When a homogeneous crystal is excited by quanta or particles a certain number of electrons and positive holes becomes free to move in an applied electric field. Thereby the crystal is made conducting. The conductivity σ of the crystal for uniform density of excitation throughout its volume is given by

$$\sigma = e(b_n n + b_p p) \tag{1}$$

where e is the electronic charge, n the number of conduction electrons and b_n their mobility, p the number of positive holes and b_p their mobility. This conductivity can be obtained by measurements of photocurrent and voltage provided that the electrodes used make good ohmic contacts with the crystal surface.

The freed electrons and holes finally lose their energy by luminescence emission or by thermal dissipation (non-radiative transitions). In the following theory we assume that recombination of conduction electrons with holes trapped in defect centres which are normally occupied (i.e. at 0° K in the unexcited crystal) gives rise to luminescence, the centres being denoted as *activator* centres. Some phosphors have centres involving other transition mechanisms[17] but for mathematical treatment some definite assumption about the luminescence transition is necessary. The above assumption is, however, applicable to ZnS . CdS type phosphors with monovalent activators (Cu, Ag, etc.). Therefore the number of activator atoms A is assumed equal to the number of electrons available from normally occupied defect levels and is determined by the Fermi distribution limit at 0° K, i.e.

$$A = \int_{E_v}^{\xi_0} S_E dE \tag{2}$$

where S_E is the number of defect levels per unit energy range,

E_v is the energy position of the top of the valency band and ξ_0 is the position of the Fermi limit. The luminescence intensity L is then given by

$$L = n\int_{E_v}^{\xi_0}\beta(S_E - s_E)dE \tag{3}$$

where β is the recombination coefficient for electrons and empty centres, and the integral is the number of empty centres, s_E being the number of occupied centres per unit energy range, obviously a function of the number of electrons and positive holes. The number of trapping states is given by the number of defect levels lying above the Fermi limit

$$H = \int_{\xi_0}^{E_L} S_E dE \tag{4}$$

and the number filled by

$$h = \int_{\xi_0}^{E_L} s_E dE \tag{5}$$

E_L being the energy position of the bottom of the conduction band. Neutrality conditions give

$$n - p = \int_{E_v}^{\xi_0}(S_E - s_E)dE - \int_{\xi_0}^{E_L} s_E dE \tag{6}$$

To the above equations we must add those governing electronic transitions between the various bands and levels. The time dependence of electrons and holes can be expressed thus

$$dn/dt = Z - n\int_{E_v}^{E_L}\beta(S_E - s_E)dE + \int_{E_v}^{E_L}\delta s_E dE \tag{7}$$

$$dp/dt = Z - p\int_{E_v}^{E_L}\alpha S_E dE + \int_{E_v}^{E_L}\gamma(S_E - s_E)dE \tag{8}$$

where Z is the excitation intensity (number of electrons raised to the conduction band per sec per cm^3).

Direct transitions between conduction band and filled band and transitions between defect levels have been neglected. The transition coefficients α, β, γ and δ are usually dependent on the energy state of a defect level. From equations (6), (7) and (8) we obtain the dependence of the number of electrons in defect levels on the time

$$ds_E/dt = \beta n S_E(1 + \gamma/\beta n) - \beta n s_E(1 + \alpha p/\beta n + \delta/\beta n + \gamma/\beta n) \tag{9}$$

For steady state conditions ($ds_E/dt = 0$) we have the distribution

$$s_E/S_E = [1 + (\alpha p + \delta)/(\beta n + \gamma)]^{-1} \tag{10}$$

In the absence of excitation equation (10) must correspond to the Fermi distribution[3]

$$s_E/S_E = \{1 + (F/n)\exp[-(E_L - E)/kT]\}^{-1} \tag{11}$$

where $F = 2(2\pi mkT/h^2)^{3/2}$

The values of β and δ and of α and γ are therefore interrelated thus

$$\delta = \beta F\exp[-(E_L - E)/kT] \tag{12}$$

$$\gamma = \alpha F\exp[-(E - E_v)/kT] \tag{13}$$

Following solid state theory[3,18] we assume that

$\delta = \delta_0\exp[-(E_L - E)/kT]$ and $\gamma = \gamma_0\exp[-(E - E_v)/kT]$

and conclude that, with respect to equations (12) and (13), α and β vary only slowly with E. Here we assume them to be constant.

Using the equations (6), (12) and (13) we may simplify equations (7) and (8) to give

$$dn/dt = Z - \beta n(n + H - p) + \beta n\int_{E_v}^{E_L}(F/n)s_E\exp[-(E_L - E)/kT]dE \tag{14}$$

$$dp/dt = Z - \alpha p(p + A - n) + \alpha p\int_{E_v}^{E_L}(F/p)(S_E - s_E)\exp[-(E - E_v)/kT]dE \tag{15}$$

These equations together with equation (9) give general mathematical expressions for finding the electron and hole concentrations, and therefore for finding the luminescence and photoconductivity characteristics from the energy states and their electron population in the phosphor. As the general solution of these equations is very difficult we apply them here to a specific and simple case in order to obtain equations easy to compare with experimental results.

LUMINESCENCE AND PHOTOCONDUCTIVITY IN CRYSTALS OF HIGH LUMINESCENCE EFFICIENCY

A high light yield is present if the number of radiationless transitions is small. Then for steady state excitation of density Z

$$L = Z \tag{16}$$

as well as

$$n \gg p \quad \text{and} \quad \beta n \gg \alpha p \tag{17}$$

Equation (1) for the conductivity then becomes

$$\sigma = eb_n n \tag{18}$$

If there is no thermal dark current, i.e. $E_L - \xi_0$ is large, we obtain from equations (9) and (14)

$$\frac{dn}{dt} + \int_{\xi_0}^{E_L}\frac{ds_E}{dt}\cdot\frac{dE}{1 + (n/F)\exp[(E_L - E)/kT]} = Z - \beta n(n + H) + \beta n\int_{\xi_0}^{E_L}\frac{S_E dE}{1 + (n/F)\exp[(E_L - E)/kT]} \tag{19}$$

To solve equation (19) we still need to know the variation of S_E with E between ξ_0 and E_L (trap distribution) for the given crystal; also we need a method for calculating ds_E/dt. Although in some cases a single level for perturbation centres is assumed we shall assume S_E to vary but slowly with E (cf. Randall and Wilkins[19]) in order to simulate more closely an experimental condition sometimes encountered. To calculate ds_E/dt we assume equilibrium between conduction band electrons and those in traps to be attained very quickly even in the non-steady case. This follows the precedent of Fröhlich[20] for treatment of dielectric breakdown in solids, and of Rose[15] for the photoconductivity of CdS crystals with various trap distributions. Therefore we assume that the relation between s_E, n and T is valid, as given in equation (11), in the steady and in the non-steady states, and we have

$$\frac{ds_E}{dt} \simeq \frac{ds_E}{dt}\left(\begin{matrix}\text{steady}\\ \text{state}\end{matrix}\right) = \frac{S_E\cdot F/n\cdot\exp[-(E_L - E)kT]}{\{1 + (F/n)\exp[-(E_L - E)/kT]\}^2}\left(\frac{1}{n}\frac{dn}{dt} - \frac{(E_L - E)}{kT^2}\frac{dT}{dt}\right) \tag{20}*$$

* By an estimation not given here it can be shown that equation (20) holds for most cases of decay or glow curves but not for fluorescence and conductivity rise curves.

and by integration of equation (19)

$$\frac{dn}{dt}\left(1+\frac{S_E kT}{2n}\right)-\frac{dT}{dt}\frac{S_E k}{2}\log\frac{F}{n} = Z-\beta n\left(n+H-S_E kt\log\frac{F}{n}\right) \quad (21)$$

Equation (21) represents a differential equation which shows for crystals of high luminescence efficiency the relation between concentration n and the excitation intensity Z, temperature T and time t. From this the conductivity $\sigma(n)$ (equation 18) and the luminescence $L(n)$ (equations 3, 5, 6 and 11) can be described for all steady and non-steady states.

which gives the relation of conductivity to excitation intensity or to the luminescence. When n is small we have

$$\sigma=\frac{eb_n Z}{\beta\left(H-S_E kT\log\frac{F}{n}\right)}=\frac{eb_n L}{\beta\left(H-S_E kt\log\frac{F}{n}\right)} \quad (24)$$

The relations of equations (23) and (24) agree well with experimental observations[14] (Fig. 1(*a*) and Fig. 2). The dependence on temperature is mainly determined by the decrease of mobility with temperature (Fig. 3). In experiments an increase of conductivity with temperature is some-

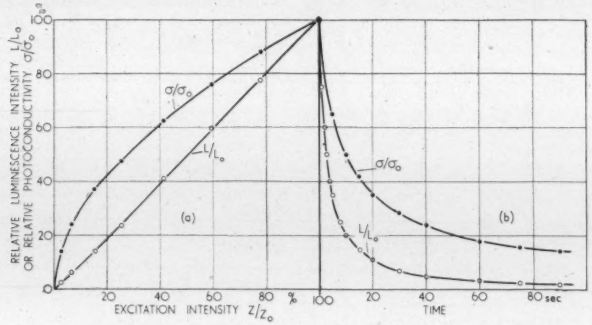

Fig. 1. Luminescence L and conductivity σ of a ZnS crystal as a function of (*a*) excitation intensity and (*b*) time. (Excitation $Z \simeq 10^{15}$ electrons/cm^3, $\lambda = 3650$ Å.)

(*a*) *Dependence of conductivity* (σ) *on luminescence* (L), *excitation intensity* (Z) *and temperature* (T) *for steady conditions.* From equation (21) we have for the steady state, $(d../dt = 0)$

$$n=-\frac{H-S_E kT\log\frac{F}{n}}{2}\pm\sqrt{\left[\tfrac{1}{4}\left(H-S_E kT\log\frac{F}{n}\right)^2+\frac{Z}{\beta}\right]} \quad (22)$$

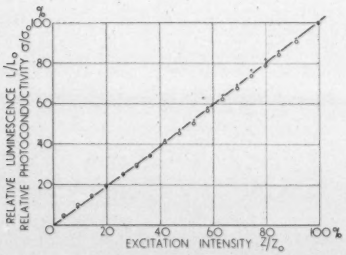

Fig. 2. Luminescence and conductivity of a CdS crystal as a function of excitation intensity. (Excitation $Z \simeq 10^{11}$ electrons/cm^3, $\lambda = 5461$ Å.)

The factor $\log(F/n)$ will not change much even for large variations of n and may be regarded as constant and of the order of 10 to 20. When n is large then $[H - S_E kT \log(F/n)] \ll \sqrt{(Z/\beta)}$ and from equation (22) it follows that

$$\sigma = eb_n\sqrt{(Z/\beta)} = eb_n\sqrt{(L/\beta)} \quad (23)$$

times observed[14] for weak excitation. This follows from equation (24) if the decrease in the denominator with temperature is at a greater rate than the change of mobility with temperature. In different crystals the number of traps is different and so even for the same light yield different values of conductivity result, as predicted by equation (24).

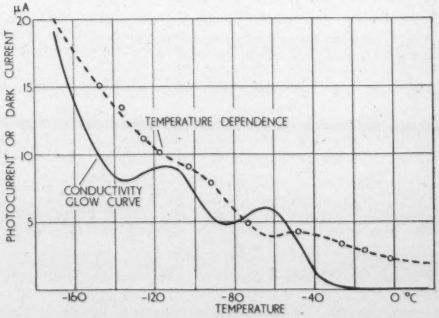

Fig. 3. Heating curve and temperature dependence of conductivity of a CdS crystal. (Excitation by γ-rays, $Z = 1{\cdot}6 \times 10^{11}$ electrons/cm^3.)

(*b*) *Decay and glow curves.* For non-steady states equation (21) also leads to a relatively simple result, though the calculation includes retrapping and non-saturated filling

of traps.[18,19] During decay at constant temperature and for small n values we have

$$\frac{dn}{dt}\frac{S_E kT}{2n} = -n\beta\left(n + H - S_E kT\log\frac{F}{n}\right) = -nf(n) \quad (25)$$

which has the approximate solution

$$nf(n) = Z_0 \Big/ \left(1 + \frac{2Z_0 t}{S_E kT}\right) \quad (26)$$

where Z_0 is the excitation intensity at $t = 0$. The function

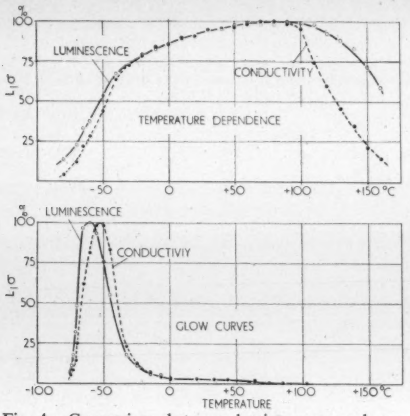

Fig. 4. Comparison between luminescence and conductivity of a ZnS crystal for different temperatures. (Excitation $Z\ 1 \simeq 0^{13}$ electrons/cm^3, $\lambda = 3650$ Å.)

is given by $nf(n)$, and replace $f(n)$ by the ratio Z/n_Z of equation (27) then we have

$$\frac{L_t}{Z_0} = \frac{Z_t}{Z_0} = 1 \Big/ \left(1 + \frac{2Z_0 t}{S_E kT}\right) \quad (28)$$

where L_t is the luminescence intensity at time t after cessation of the excitation (intensity Z_0), and $Z(t)$ is the number of electrons escaping from the traps into the conduction band. The function $\sigma(t)$ we obtain by eqns. (23) and (24) replacing Z by $Z(t)$.

Luminescence and photoconductivity thus show the same

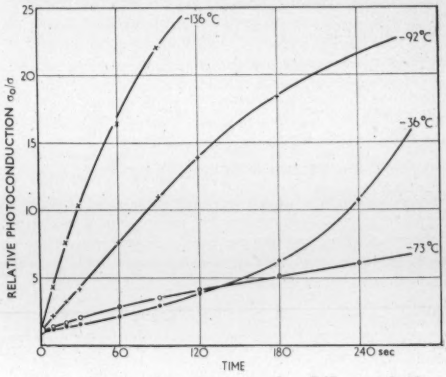

Fig. 5. Decay of conductivity of a CdS crystal (the same crystal as in Fig. 3) for different temperatures. (Excitation by γ-rays, $Z = 1{\cdot}6.10^{11}$ electrons/cm^3.)

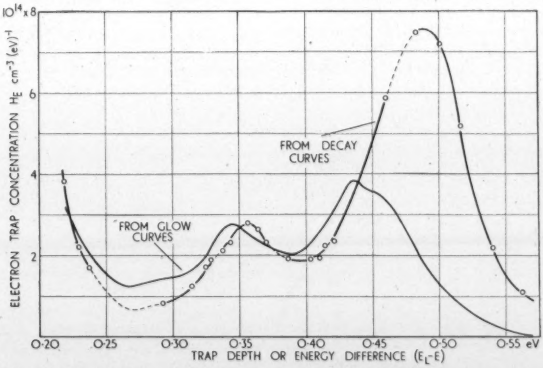

Fig. 6. Distribution of traps for a CdS crystal calculated from decay curves (Fig. 5) and from heating curves (Fig. 3). (The discrepancy between the curves at higher energy values might be due to radiationless transitions in the warming case.)

$f(n)$ represents the amount of departure from the simple bimolecular law of recombination and can be found from the variation of n with intensity Z

$$f(n) = Z/n_Z \quad (27)$$

where n_Z is the value of n under steady excitation Z.

If we assume that to a first approximation the luminescence type of decay if their steady state values both vary linearly with excitation intensity. In other cases they differ according to the difference in the steady state variations [Fig. 1(*b*)].

To consider the glow (or heating) curves for luminescence and conductivity, equation (21) is written in the form

$$\frac{dT}{dt}\frac{S_E k}{2}\log\frac{F}{n} = n\beta\left(n + H - S_E kT\log\frac{F}{n}\right) = nf(n) \quad (29)$$

assuming no large fluctuations in n during heating. This is so if S_E varies but slowly with E, and if on commencing heating large variations in n are prevented (see below). In this case we obtain from equation (21)

$$\frac{L_t}{Z_0} = \frac{\sigma_t}{\sigma_T} = \frac{k}{2Z_0}\frac{dT}{dt} \cdot S_E \log \frac{F}{n} \tag{30}$$

where σ_t is the conductivity during warming at time t and temperature T and σ_T is the conductivity obtaining at temperature T for a steady state excitation there of intensity Z_0. The curves of luminescence and conductivity are thus related at any temperature by a given factor which is determined by their temperature dependence under steady state conditions (Fig. 4). Large values of L_t and σ_t occur for high rates of heating and for large trap concentrations. To ensure only small variations in n the heating rate must be chosen so that $dn/dt = 0$. This will be so if

$$\frac{dT}{dt} = \frac{2Z_0}{S_E k T}\frac{T_0}{\log (F/n)} \tag{31}$$

The optimal heating rate can be obtained from decay measurements at T_0, according to equation (28).

(*c*) *Determination of trap distributions from decay and glow curves.* Equations (28) and (30) are approximately valid if S_E does not change much with E. This has been found to be true for a great number of crystalline phosphors. Then in equations (28) and (30) S_E formally is a function of t or T. From glow and decay experiments (Figs. 3 and 5), showing deviations from the form of curves calculated with $S_E =$ constant, it is possible to find the connexion between S_E and t or T.

On the other hand there is an approximate correlation between the energy-difference $E_L - E$ and the time or temperature. The largest variation of the electron concentration s_E occurs at the inflexion point of the Fermi distribution (energy E_ζ) given in equation (11). At time t equivalent to temperature T those traps will be emptied which are near this Fermi level. For each value t or T there is a corresponding energy difference $E_L - E_\zeta$ which can be obtained from equation (11)

$$E_L - E = kT(t) \log [F/n(t)] \tag{32}$$

where $T(t)$ is the temperature and $n(t)$ the number of conduction electrons at time t during decay or heating experiments. Equations (28) and (30) solved for S_E and equation (32) give parametric relations between S_E and E, which can be fitted to the experimental curves to give absolute values of S_E and E if the absolute values of Z and n are known (Fig. 6).

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DISCUSSION

Dr. D. Curie: Equation (3) of Paper 17 suggests a bimolecular mechanism. It might be that this holds in photoconduction, electroluminescence or infra-red stimulation (high energy electrons), but that a monomolecular law holds for thermally excited electrons (phosphorescence or glow). In actual cases the two processes must be mixed.

Dr. G. Diemer: Trap distribution and mobility data are important in theories of electroluminescence. Is there a physical explanation why the trap density in ZnS is about 1000 times larger than in CdS? What is the value of the electron mobility for ZnS from your measurements?

Authors' reply: In reply to Dr. Curie, equation (3) describes only the recombination process between conduction band and activator. It is generally valid and does not depend on the process by which the electron concentration is produced, whether thermally or by radiation.

In reply to Dr. Diemer, it is easier to grow CdS crystals with a small number of traps than ZnS crystals, which is partly due to the lower temperature used for the crystal growth and the higher thermal conductivity of CdS. Crystals of CdS with a much higher trap concentration can, of course, also be produced easily. We have no final results for the electron mobility in ZnS.

Paper 18

Use of radioactive isotopes for research on inorganic phosphors

By E. GRILLOT and M. BANCIE-GRILLOT, Laboratoire de Luminescence, Faculté des Sciences de Paris

The radioactive tracers are of great interest for controlling the efficiency of purification of raw materials. Moreover, the action of thermal neutrons on inorganic phosphors may be used for microdeterminations, not only of activator elements such as copper, but also of halogens.

The preparation of inorganic crystalline luminescent substances requires, in principle, first the maximum elimination of extraneous elements, and then the reincorporation of some of them, or others, in precise amounts. Concerning the activator or "killer" impurities which are effective at very small concentrations (sometimes lower than 10^{-6}), control of the efficiency of the purification method sets problems which classical processes of chemical or spectrographic microanalysis are not always able to solve. In such cases it is only possible to obtain empirical information from the luminescent properties of the final substances themselves. The purification is, moreover, always followed by treatments such as the action of certain gases, or heating at high temperatures: during these treatments, the possibility of involuntary reintroduction of impurities must not be ignored.

As far as the deliberate addition of foreign impurities is concerned, the only information generally given is the proportion in which they have been added to the base material before heating, and also the temperature at which heating has taken place. It would be preferable to know the precise amount actually incorporated in the lattice, and even its distribution. For the smallest amounts, chemical analysis is not capable of providing such information.

Under these circumstances, it appears that the improvement of preparative methods for phosphors can only be generally obtained if the sensitivity of microanalysis of traces of impurities is increased. This is also necessary in the investigation of reaction mechanisms, for example, the diffusion of atoms of impurities through the lattice. In certain cases, these objects may be achieved by the use of radioisotopes.

In practice each particular investigation provides its own technical questions, sometimes very difficult ones. But the principle of the use of radioisotopes in this kind of microanalysis is very simple. For example, control of the efficiency of a purification process with respect to a given element may be operated by introducing a small amount of this element labelled with one of its radioactive isotopes, and then examining how its elimination is accomplished. If, on the contrary, the problem is the quantitative microanalysis of one element included in a solid (a raw material or a sample taken at some stage of a process), this solid may be directly exposed to the action of a nuclear reactor. Then, among other products, a radioisotope of the element sought (or of a neighbouring one) is produced, in amount proportional to the concentration of the impurity. After separation by chemical means, it is possible to calculate this concentration by comparison of the activity with standards prepared from pure compounds containing the same element, exposed for the same time to the same bombardment.

The value of such methods varies considerably from one element to another. It will increase as the specific activity increases and when the indispensable chemical separations are easier, taking also into consideration the law of decay of activity. Using the Chatillon atomic pile (Zoe) as nuclear reactor, it is hoped to increase by this method the sensitivity of detection of those elements which have non-radioactive isotopes with the following characteristics:

(1) sufficient abundance in natural substances,
(2) reactivity (n, γ) to thermal neutrons with sufficiently large cross-section,
and (3) formation by this reaction of radioactive isotopes with half-life from one hour to a few days.

One important activator in phosphors is copper, a metal for which sensitive colorimetric reactions are available, for example, down to 10^{-6} g.-ion per litre with sodium diethyldithiocarbamate. If the problem is the quantitative microanalysis of copper in zinc sulphide, the limit of detection is 3×10^{-6} g Cu per g Zn, reached with difficulty. The spectrographic technique reaches approximately the same limit, hence it appears that for copper concentrations equal to or less than one part per million, at which the activating effect of this metal is still evident, chemical and spectrographic methods will not even detect the presence of copper.

Electrolysis has been proposed as a method for purifying zinc salts from copper. But it is not impossible that copper, always present in platinum electrodes, could be brought into solution. For this reason, the method has been replaced by the spontaneous discharge of copper ions upon metallic zinc.[1, 2] To determine whether the method gave complete removal of copper, the following experiment was performed. Pure copper sulphate was submitted to the maximum flux of thermal neutrons in the Chatillon pile. Very small amounts were then introduced into solutions of various concentrations of zinc sulphate. These solutions were boiled with pure metallic zinc, and the variation of copper concentration with time determined by treating aliquot parts with successive additions of non-radioactive copper ions (about 1 mg), in order to deposit all the radioactive ^{64}Cu on one face of a small disk of zinc. Thus it was clearly shown[3] that the spontaneous discharge of copper ions does not exceed a limit of about 2×10^{-6} g.-ion Cu per litre. Since accidental additions of copper could only have the effect of decreasing the residual radioactivity of the solution, the measured limit is unquestionable. With a volume of solution as small as 20 ml, the observed radioactivity, due solely to the radioactive copper remaining in the solution, was of the order of 600 counts per minute recorded by a Geiger-Müller counter 12 hours after irradiation in the pile.

At any moment during the decay of its activity, the limit of detection of a radioactive element may be taken as 15% of the background of the counter. Twelve hours after irradiation, this limit for copper corresponds to 10^{-8} g Cu containing its radioactive isotope 64. This very great sensitivity has been used for the quantitative microanalysis of copper included in the lattice of a crystal.[4, 5] By irradiation of 10 g of this solid in the maximum flux of thermal neutrons in the Chatillon pile, it became possible to detect 10^{-9} g Cu per gram. of solid. Radioactive copper was separated by classical methods from other radioactive elements produced

by the action of neutrons on the basic substance. Measurements of the half-life and of absorption of the radiation by screens proved that it was solely due to radioactive ^{64}Cu. Naturally only the copper contained in the solid during irradiation may be so detected.

As far as the solid compounds of zinc are concerned, this radiochemical method for copper may be questioned, since a (n, p) reaction from the stable isotope 64 of zinc to the radioactive isotope 64 of copper has been observed.[6,7] In fact the cross-section for the reaction is extremely small,[8] but if the reaction does occur, the radioactive copper 64 would be formed in addition to that from the (n, γ) reaction of copper 63 in the solid. It is therefore necessary to ascertain the efficiency of this (n, p) reaction produced by thermal neutrons. If this question could be settled, the problem of the light blue fluorescence of "absolutely pure" zinc sulphide might perhaps be solved more readily than by available methods.

Another important problem is the mechanism of diffusion of activating impurities into the lattice of crystals. In the case of zinc sulphide prepared with a chloride flux, it has been shown of interest to compare the concentration of chlorine actually incorporated in the lattice with that of activator centres.[9] Unfortunately, the nephelometric method of determination of chlorine gives only an order of magnitude. But the use of radioactive chlorine shows that the nitrogen oxides produced during the reaction of zinc sulphide with 4 *N* nitric acid carry away a variable and often important fraction of the chlorine to be estimated.[10]

It is well known that the stable isotope 37 of chlorine (abundance 24·6%) gives by (n, γ) reaction a radioactive chlorine 38 with a relatively short half-life (37·2 min). Even in this case, the radiochemical microdetermination of chlorine in zinc sulphide phosphors may give better results than the nephelometric one.[10] Provided that the whole of the separation of radioactive chlorine from all other radioactive elements formed at the same time is completed within three hours of the end of the irradiation, the sensitivity of the method reaches 10^{-6} g Cl per gram ZnS; the accuracy is better than 10%, for chlorine contents varying between 10^{-5} and 5×10^{-5}.

Other elements, such as the rare earths, seem to admit of much greater sensitivity of detection than chlorine or copper. The examples given above are sufficient to suggest the improvements that might result from a more general application of the radiochemical technique to other elements which are important in the luminescence of inorganic crystals.

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DISCUSSION

Dr. F. E. Williams: On the subject of radioactive isotopes in luminescence research, an experiment now being carried out by Prener of our laboratory has the purpose of providing information on the controversial subject of the nature of the activator systems in ZnS.Cu. Prener has prepared pure ZnS containing about 10^{-3} mole per cent of radioactive Zn^{65}, which by K-capture transforms in 240 days to Cu. The recoil energy of the nuclear reactions is insufficient to displace any appreciable fraction of the Cu from the Zn sites. The changes in the luminescence properties are being measured as the transmutation progresses.

Dr. P. Brauer: The question why one activator prefers one host lattice and can scarcely enter another, or why another activator has the reverse behaviour (for instance, why Tl enters KCl but not NaCl, while Mn shows the opposite effect) also requires consideration. I believe that the use of radioactive isotopes will help in this problem.

Authors' reply: The interest in radioactive isotopes increases with the concentration they reach in other solids. Even when this concentration is relatively low (for example 10^{-10} radioactive Cu in Cu) new methods of investigation become available, leading to a better knowledge of the chemical constitution of phosphors. Concerning the formation of radioactive Zn^{65} from Zn^{64} under the action of thermal neutrons, the cross-section is ten times smaller than that of formation of radioactive Cu^{64}. Thus we could not hope to obtain a concentration larger than 10^{-11}.

Radioisotopes have been used to examine the mechanism of diffusion of various impurities into phosphors, and may help to determine whether certain impurities do not enter the lattice or whether they enter in small amounts but without affecting the luminescence. Radioactive Mn (with a period of 2½ hours) may be used for this. Isotopes of Tl might be useful, but unfortunately have periods that are either too long or too short.

Paper 19

Theory of activator systems in luminescent solids

By F. E. Williams, Ph.D., General Electric Research Laboratory, Schenectady, N.Y., U.S.A.

The theory of localized activator systems in ionic phosphors is reviewed. The monovalent thallium and divalent manganese activator systems are treated quantitatively in detail. The importance of the nonspherical symmetry of the electron distribution of excited Tl^+ and Mn^{2+} is emphasized. The excitation and emission spectra are evaluated both classically and quantum mechanically from the energies of the accessible atomic configurations of the activator system in the ground and emitting states, respectively. The origin of the fine structure of emission of the tetravalent manganese activator systems is discussed. Modifications in the theory are proposed for covalent luminescent solids such as the zinc sulphide phosphors.

A quantitative theory of solid state luminescence has been developed and applied to impurity-activated ionic crystals.[1] From fundamental considerations and the properties of the constituent ions, the theoretical absorption and emission spectra of thallium-activated potassium chloride have been evaluated and found to be in satisfactory agreement with experiment. The spectra at low temperatures have also been determined by including the effect of the quantum mechanical zero-point energy.[2,3] More recently, the theory of activator systems has been improved by taking into account the angular dependence of the wave functions of excited states of the activator ions, and preliminary results on potassium chloride activated with divalent manganese have been reported.[4] In the present paper, the theory will be formulated in general and applied to diverse activator systems in both ionic and covalent phosphors.

THEORY OF LOCALIZED ACTIVATOR SYSTEMS IN IONIC CRYSTALS

The theory will be formulated for impurity-activated ionic crystals having localized electronic wave functions for the activator ions in both the ground and excited states. To determine the degree of tight binding character of the activator ion A^{+a} in the electronic state n in the solid MX, the following cycle proposed by Johnson and Williams[5] is utilized:

$$\begin{array}{ccc} A_n^{+a}(g)+MX(s) & \xrightarrow{-I} & A_0^{+a+1}(g)+MX(s)+e \\ \downarrow \Delta E & & \uparrow -\Delta E'+F \\ MX.A_n^{+a}(s)+M_0^{+a'}(g) & \xrightarrow{I^*} & MX.A_0^{+a+1}(s)+M_0^{+a'}(g)+e_f(s) \end{array} \tag{1}$$

where I is the ionization energy of the gaseous ion A_n^{+a}, F is the electron affinity of the MX crystal in the lowest conduction state, and I^* is the ionization energy of A_n^{+a} in the solid $MX.A$ and is, therefore, a measure of the degree of tight binding. The changes in total energy ΔE and $\Delta E'$ arising from substituting A_n^{+a} and A_0^{+a+1}, respectively, for $M_0^{+a'}$ in MX must be computed. Madelung, exchange repulsion, van der Waals, and ion-induced dipole energies are included. If n is an excited state, the polarizability and ionic radius of A_n^{+a} and the compressibility of A_n^{+a} interacting with $X^{-a'}$ must be evaluated theoretically from radial charge densities. The perturbation of the electronic energy of $A_n^{+a}(g)$ by the local crystal potential is also included in ΔE and $\Delta E'$. The first-order perturbation in the energy is:

$$\delta E_n = e\int \phi_n^* \delta V \phi_n dv \tag{2}$$

where δV is the difference between the local potential and the potential at the lattice point, and ϕ_n is the unperturbed electronic wave function of the nth state of $A^{+a}(g)$. If I^* is at least several electron volts for the excited state of A^{+a}, then, it may be concluded that highly localized wave functions and atomic rearrangements are involved in the luminescence of $MX.A$.

The substitution of the unexcited activator ion A_0^{+a} for $M_0^{+a'}$ in the lattice of MX creates a local atomic distortion with the interacting neighbouring ions shifted to new equilibrium positions. Following excitation, the excited activator ion A_1^{+a} is not in equilibrium with the lattice. The A_1^{+a} interacts differently from the A_0^{+a} with the nearest neighbours $X^{-a'}$. The lifetime of the excited state is sufficiently long for equilibrium to be re-established with the neighbours displaced to new positions of minimum potential energy. Because of the localized character of the wave functions of the A_n^{+a} in both the ground and excited states, only the interactions of the A_n^{+a} with the $X^{-a'}$ nearest neighbours are peculiar to the electronic state of the A_n^{+a}; therefore, restricting the atomic rearrangements to appropriate displacements, radially from the A_n^{+a}, of the nearest neighbours and displacing all other ions to positions of minimum potential energy, the change in energy is a function of only one variable. The change in total energy of the system is calculated for various atomic configurations. For small displacements from the equilibrium configuration for a given state A_n^{+a}, the energy change is found to be a quadratic function of the configuration co-ordinate.

From the quantitative dependence on the configuration co-ordinate of the total energy of the activator system in both the ground and the excited states, the luminescent spectra can be calculated either classically or quantum mechanically. The classical formula for the absorption or emission spectrum is:

$$P(\xi) = (K/2\pi kT)^{1/2} e^{-Kq^2/2kT}(dq/d\xi) \tag{3}$$

where q is the displacement in the configuration co-ordinate from the equilibrium configuration for the initial state, ξ is the transition energy at q in accordance with the Franck–Condon principle, and K is the force constant for the initial state.

The quantum mechanical zero point energy must be considered in deriving the spectrum at low temperatures. Assuming that the normal modes of motion which involve appreciable changes in the potential energy of the activator system are approximated by an Einstein distribution, it is evident that the system is a harmonic oscillator with the vibrational levels:

$$E_i = \hbar(K/M)^{\frac{1}{2}}(i+1/2) \tag{4}$$

where M is the effective mass of the appropriate number of $X^{-a'}$ nearest neighbours coupled to the remainder of the

lattice. The quantum mechanical spectrum will consist, therefore, of a series of lines:

$$P(\xi_{if}) = C\left[\int \psi_i \psi_f dq\right]^2 e^{-E_i/kT} \qquad (5)$$

where ξ_{if} is the transition energy from the vibrational level i of the initial state to the level f of the final state, and ψ_i and ψ_f are, respectively, the vibrational part of the wave functions of the initial and final states. The electronic part of the wave functions is assumed to be independent of the configuration co-ordinate and is, therefore, integrated out and included in the normalization constant C.

APPLICATION OF THE THEORY TO IONIC PHOSPHORS

The activator system for KCl . Tl is shown in Fig. 1. The Tl^+ has replaced a K^+ at the centre of the cube. The Cl^- in the centres of the cube faces have markedly different

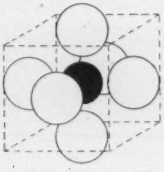

Fig. 1. Activator system for KCl . Tl

interaction energies for different electronic states of the Tl^+. Energy and transition probability considerations suggest that the 2460 Å absorption and the 3050 Å emission bands of KCl . Tl arise from the $^1S_0 \rightleftarrows {}^3P_1^0$ transitions. The ground and excited states have the $1s^2 \ldots 5d^{10}6s^2$ and $1s^2 \ldots 5d^{10}6s6p$ electronic configurations, respectively. The radial charge densities of the 6s and 6p electrons of free $^1S_0$ and $^3P_1^0Tl^+$ have been evaluated by the Hartree self-consistent field method and are shown in Fig. 2 along with the total radial charge densities for these ions. For both states the wave functions are quite localized. Evaluation and substitution of ΔE and $\Delta E'$ in equation (1) yield for the $^1S_0$ and $^3P_1^0$ states, respectively, 9·5 and 5·0 eV for I^*. The band theory model of KCl . Tl for equilibrium atomic configurations for each electronic state is shown in Fig. 3. For comparison the energy levels of F- and V-centres are also shown. In the calculation of interaction energies, both for evaluation of the degree of tight binding and for the determination of the configuration co-ordinate diagram, the effects of the angular dependence of the wave function for the excited state on minimizing the exchange repulsion energy and on enhancing the perturbation by the local crystal field are included. The lobes of the 6p orbital can be oriented along the face diagonals of the activator system shown in Fig. 1 so that the repulsion energy of interaction of the 6p electron with the ions of the crystal is negligible and the local electrostatic field increases the binding energy of the $^3P_1^0$ state of Tl^+. The perturbation is calculated by equation (2) using the local crystal field shown in Fig. 4 evaluated by the method of Ewald.[6] The configuration co-ordinate diagram of the activator system for KCl . Tl is shown in Fig. 5. The abscissa is the symmetric displacement of the six nearest Cl^- neighbours from the perfect KCl lattice sites. All other ions are simultaneously moved to positions of minimum potential energy. The points are computed from the detailed interaction energies. Representative vibrational levels and wave functions are also shown. The experimental spectra and the theoretical spectra evaluated from equation (3) are shown in Fig. 6 for 298° K. Other neglected co-ordinates broaden the lines predicted by equation (5), however, smoothing the theoretical spectra results in agreement with the experimental absorption spectrum at 4° K reported by Johnson and Studer.[7]

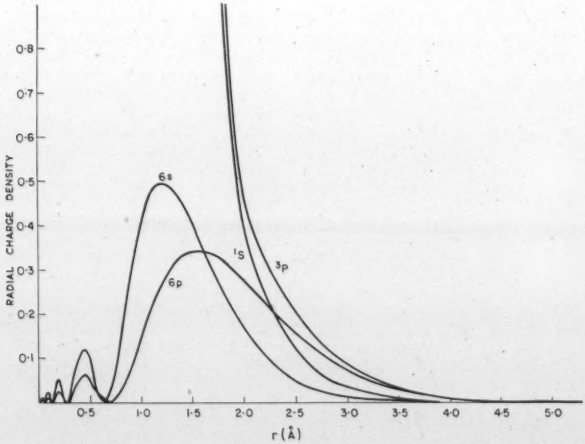

Fig. 2. Radial charge densities of ^1S and $^3P_1^0Tl^+$ and of the individual 6s and 6p electrons

The activator system for KCl . Mn is similar to Fig. 1 except that the divalent manganese occupies the centre of the unit cell and a cation vacancy occupies another K^+ site remote from the activator system. Magnetic susceptibility measurements have shown that the unexcited Mn^{2+} is in the

^6S state with the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ and with the five 3d electrons having the same spin. Calculation of the difference in energy arising from substituting ^6S Mn^{2+} and Mn^{3+} at K^+ sites in KCl and substitution in the cycle described in equation (1) reveal that the ionization energy I^* of ^6S Mn^{2+} in KCl is approximately 20 eV. The wave functions of the outer shell electrons of the activator ion are, therefore, quite localized; and the configuration co-ordinate model should be particularly applicable. Theoretical

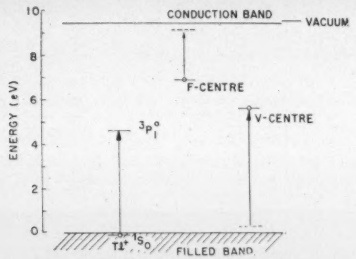

Fig. 3. Band theory model for KCl . Tl

calculations, assuming that the excited state has the . . $3d^4 4s$ or . . $3d^4 4p$ electronic configuration of Mn^{2+}, yield transition energies too large for the experimental emission spectrum. Excitation to states having the same principal and orbital angular momentum quantum numbers for the individual electrons as the ground state, but having a change in multiplicity or electron spin were considered. The ^4P Mn^{2+} which has the spin of one of the $3d^5$ opposite to the other four was examined in detail. A Hartree–Fock calculation which

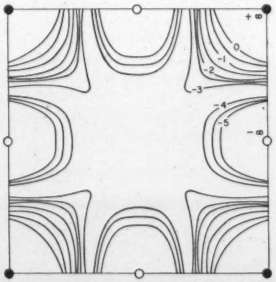

Fig. 4. Electrostatic potential in the 100 plane of the rock-salt lattice with a cation vacancy. Equipotential lines in units of Q/d_0, where Q is the charge on the ions and d_0 is the unit cell dimension

includes the effect of exchange interaction between the 3d electrons of the same spin was necessary to evaluate the radial charge densities of the free ^6S and ^4P Mn^{2+}. The ^4P Mn^{2+} is non-spherically symmetrical and the four directions in which there is a deficiency of charge of the same spin can be directed to minimize the exchange repulsion interaction with the four Cl^- neighbours in a plane in KCl. The other two Cl^- neighbours experience very nearly the same interactions with the ^4P Mn^{2+} as with the ^6S Mn^{2+} for a given atomic configuration. The appropriate configuration co-ordinate is, therefore, the symmetric displacements, radially from the Mn^{2+}, of the four planar nearest neighbour Cl^- from the perfect KCl lattice sites. All other ions are, of course, displaced to positions of minimum potential

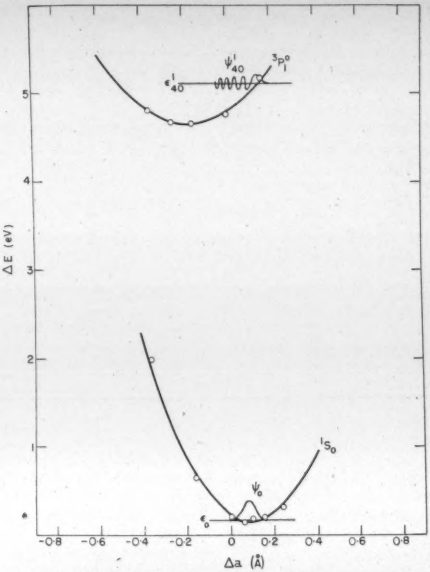

Fig. 5. Configuration co-ordinate diagram, including representative vibrational levels and wave functions, of the activator system for KCl . Tl

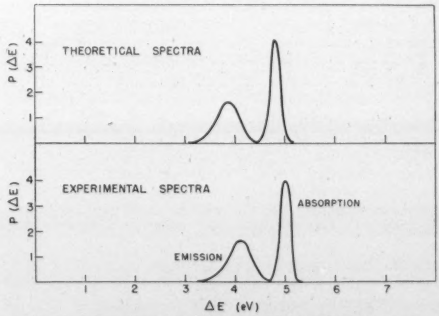

Fig. 6. Experimental and theoretical absorption and emission spectra of KCl . Tl at 298° K

energy. The theoretical emission spectrum based on the $^4P \rightarrow {}^6S$ transition is found to be in essential agreement with the experimental emission spectrum. However, the forbidden nature of the $^6S \rightarrow {}^4P$ transition combined with the cubic symmetry of the activator system for the equilibrium configuration of the ground state yield a negligible oscillator

strength for this mechanism of excitation. The identification of the ^4P state as the emitting state of phosphors activated with Mn^{2+} is in accord with the magnetic susceptibility changes accompanying excitation and emission of ZnF_2 . Mn reported by Johnson and Williams.[8]

The activator system for MgO activated with Mn^{4+} is similar to those already discussed except that $a = 4$ and $a' = 2$. Because of the large attractive Coulomb effect arising from the tetravalency, the wave functions and atomic rearrangements are localized to an extraordinary degree. It is, therefore, not surprising that the vibrational fine structure described by equation (5) is characterized in tetravalent manganese activator systems by sufficient energy separation so that multiplet structure is observable in the emission spectra.

MODIFICATION OF THE THEORY FOR COVALENT PHOSPHORS

In the case of covalent crystals activated with manganese, no important modification in the theory of activator systems appears necessary. For example, the activator system for ZnS . Mn, a covalent substance, is in many respects similar to the activator system for ZnF_2 . Mn, an ionic substance. In both materials, the electrons responsible for the luminescence are almost certainly the localized $3d^5$ electrons of the manganese. In the ground state, the spins are parallel; in the emitting state, the spin of one 3d electron is opposed to the spins of the other four. The difference between the sulphide and the fluoride is in the origin of the binding energy of the crystals. The ZnS can be considered as composed of Zn^{2-} and S^{2+} ions, both having hybridized sp^3 tetrahedral orbitals; hence, the wurtzite and sphalerite structures.[9] The substitution of manganese at zinc sites leads to similar tetrahedral orbitals, namely, Mn^{2-} (. . . $3d^5sp^3$). The ZnF_2 is, of course, clearly ionic and manganese is substituted at zinc sites as Mn^{2+} (. . . $3d^5$). The transition energy between the states of different multiplicity for the $3d^5$ electrons is quite insensitive to the valency state of the manganese; therefore, it is not surprising that the emission spectra of ZnS . Mn and ZnF_2 . Mn are practically identical. On the other hand, the transition probability which is sensitive to the symmetry of the activator system is quite different in the two materials.

In the case of zinc sulphide phosphors activated with copper, silver or gold, or self-activated, important modifications in the theory of activator systems are necessary. Kröger and his associates[10] using an ionic model for ZnS have shown that the activator can be considered as a monovalent cation at a zinc site. A monovalent anion or trivalent cation substitution is also necessary, but these impurities do not appear to be intimately associated with the unexcited activator system. Klasens[11] attributes the ground state of the activator system to a level of the valency band of ZnS which has been perturbed into the forbidden band by the monovalent activator.

For activator systems involving levels of the pure covalent substance which have been perturbed by the activator, the following cycle gives some insight into the necessary modifications of the theory:

$$\begin{array}{ccc} A^{+a}(g) + MX(s) & \xleftarrow{-E_1} & MX\,.\,A(s) + M^{+a'}(g) \\ \downarrow E_g & & \uparrow -E \\ A^{+a}(g) + [MX^*(s) + e_f(s)] & \xrightarrow{E_2+E_b} & [MX^*\,.\,A(s) + e_b(s)] \\ & & +^a M^{+'}(g) \end{array} \quad (6)$$

where E_g is the band gap in the pure covalent solid $MX(s)$, E_1 is the energy change on substituting A^{+a} at a $M^{+a'}$ site in the unexcited system, E_2 is the energy change on substituting A^{+a} at a $M^{+a'}$ site with the system in the excited state, and E_b is the binding energy to the activator system of the excited electron. To determine E, the transition energy for luminescent excitation or emission depending on whether the equilibrium atomic configuration for the ground or emitting state is used, it is necessary to know E_g and to calculate E_b and $E_2 - E_1$.

If the orbit of the excited electron is sufficiently large, the Bohr formula can be used to calculate E_b:

$$E_b = \frac{2\pi m^* e^4}{\epsilon^2 h^2} \quad (7)$$

where ϵ is the dielectric constant. There is abundant evidence that the excited activator system in ZnS . Cu and similar phosphors is spatially quite extensive. Substitution in equation (7) yields, for ZnS, E_b equal to 0·2 eV. This value agrees with experiment in magnitude and in being independent of the identity of the activator.

The calculation of $E_2 - E_1$ is more difficult. For ZnS . Cu, $E_2 - E_1$ can be considered as the difference in energy change between substituting copper for zinc in one case in the excited system; in the other case in the unexcited system. An important contribution to $E_2 - E_1$ is the ion-induced dipole interaction due to the positive hole in the unoccupied bond orbital of the excited system polarizing the activator ion differently from the zinc ion; therefore:

$$E_2 - E_1 = \frac{e^2}{2}\left(\frac{\alpha_{M^+}}{a^4} - \frac{\alpha_{Zn^{2+}}}{a_0^4}\right) \quad (8)$$

where a and a_0 are, respectively, the distance from the positive hole to the activator ion with the appropriate atomic configuration and to the zinc site with the configuration of the perfect ZnS lattice, and α_{M^+} and $\alpha_{Zn^{2+}}$ are the polarizabilities of the activator and zinc in the valency states corresponding to the removal of the bonding electrons. For ZnS . Cu, assuming for the equilibrium configuration of the ground state the same atomic configuration as the perfect ZnS lattice, $E_2 - E_1$ is equal to 0·3 eV. Substitution in equation (6) for E_b, $E_2 - E_1$, and E_g yields an excitation energy E

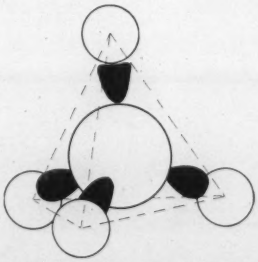

Fig. 7. Activator system for ZnS . Cu

in approximate agreement with experiment. For the excited state, the equilibrium activator nearest-neighbour distance in ZnS . Cu is greater than for the ground state because effectively only three rather than four covalent bonds are responsible for the local binding. Since the covalent bonds between the activator and the nearest-neighbour sulphur atoms are

identical for a particular electronic state of the system, the tetrahedral symmetry will be maintained. The activator system for ZnS . Cu is shown in Fig. 7. The bonding electrons have been removed from the copper and sulphur atoms to yield the spherically symmetrical ion cores Cu^{1+} and S^{6+}. The covalent bonding orbitals are strongly polarized towards the S^{6+} by the electrostatic potential distribution. Because of the localized character of the covalent bonds, the interactions which are most sensitive to the electronic state of the system are the activator, nearest-neighbour interactions. The shift of the emission spectrum to longer wavelengths compared to the absorption spectrum arises from the detailed interaction energy changes accompanying the attainment of equilibrium for the excited state.

CONCLUSIONS

A quantitative theory of localized activator systems in ionic phosphors has been developed. The activator systems for KCl . Tl and KCl . Mn are understood in considerable detail. Further detailed calculations are necessary to determine the electronic states and the configuration co-ordinate involved in the luminescence of other impurity-activated ionic crystals. The extension of the theory to covalent phosphors appears feasible. The electronic states and the configuration co-ordinate for ZnS . Cu have been tentatively identified and quantitative calculations are in progress.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the detailed calculations on KCl . Mn by Miss J. Johnston and the determination of the crystal field of Fig. 4 by Dr. J. S. Prener.

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DISCUSSION

Dr. D. Curie: The width and asymmetry of emission bands may arise from overlap of electron orbitals of different centres to form an activator band. A Gaussian band shape would by contrast indicate no interaction between centres but differences in individual centre configurations. Overlap effects for donors in germanium considered by Seitz and by Aigrain are relevant to this problem.

Dr. K. H. Butler: A more general theory of fluorescence for lamp phosphors can be based on the following hypotheses:

(1) Activators substitute for cations of the matrix.

(2) There is a one to one correspondence between energy levels of the free activator ions and the same ions in the solid.

(3) Splitting of energy levels is not of major importance.

(4) Transitions give Gaussian bands in the observed spectra.

(5) Crystal structure and cation sizes influence the energy levels of the activator.

(6) Transfer of energy from one activator to another is possible, as in sensitized luminescence.

Thallium is a specific example of a large group of useful activators, namely, those with a $d^{10}s^2$ configuration. These include atomic Hg; monovalent Ga, In, Tl; divalent Ge, Sn, Pb; and trivalent As, Sb, Bi. All these have a very similar energy level pattern, the odd levels being $^3P^0$ and $^1P^0$. The location of these above the unexcited level covers a relatively small range. Many of these elements are active in alkaline earth halophosphates and other matrices.

A preliminary study of excitation and emission spectra for KCl.Tl has given data requiring major changes in Williams' assignments of energy levels:

(*a*) The excitation band extending from 2350 to 2700 Å is found experimentally to be probably a triplet. The components represent transitions from the $6s^2$ configuration to the excited levels with $6s6p$ configuration in the $^3P_1^0$, $^3P_2^0$ and $^1P_1^0$ states.

(*b*) The excitation bands at 2060 and 1960 Å are probably due to transitions from $6s^2$ to $6s7p$, the excited states being $^3P_1^0$ or $^1P_1^0$.

(*c*) From these $6s7p$ states the excited atom can fall to the $6s6p$ configuration so that the emission is basically the same with 2000 Å excitation as with 2500 Å excitation.

(*d*) The return from the $6s6p\ ^3P_1^0$ state gives 4750 Å emission and the return from the $^1P_1^0$ state gives 3050 Å emission.

Dr. F. A. Kröger: For KCl.Mn Dr. Williams predicts an absorption band close to the emission band. Since the manganese concentration is low this will be very weak, but such a band is seen in other phosphors when the concentration is higher, and the higher excited states of Mn^{2+} are also observed.(1)

Dr. J. H. Schulman: According to von Meyeren the thallium-activated alkali bromides and iodides are very similar to the thallium-activated alkali chlorides in their absorption, but not in their emission spectra. Whereas a single emission band due to the Tl^+ ion is found in the chlorides, a double-banded emission is observed in the bromides. Irradiation in the 2610 Å absorption band of KBr.Tl, for example, produces the emission of two overlapping bands at 3180 and 3500 Å even at room temperature, and at liquid air temperature these bands are very well resolved. Analogous irradiation in the 2480 Å absorption band of KCl.Tl produces only one emission band at 2980 Å. Would the author indicate how the substitution of bromide for chloride might alter his calculations to yield the emission observed in KBr.Tl?

What is the evidence that the cation vacancy introduced by Mn^{2+} in KCl.Mn is dissociated from the Mn^{2+}?

It is no reflexion on Williams' very valuable contributions to luminescence theory to point out the following. Until transition probabilities and oscillator strengths are determined from theoretical considerations, it cannot be stated that we have an absolute theory of the luminescence centre based upon first principles. Williams is led by experiment,

not by theory, to identify the $^4P \rightarrow {}^6S$ transition in Mn^{2+} as responsible for the emission, for this transition is forbidden in the free Mn^{2+} ion, and becomes less so in the solid because of interaction of the Mn^{2+} with the crystal field.

Mr. W. A. Runciman: Using the Hartree self-consistent field method, without exchange, for all the Tl^+ wave functions, I find that the maxima of the 6*s* and 6*p* charge distributions are about 0·1 Å further out than in the approximation used by Williams. It appears to be worth while to use this and other improvements in the KCl.Tl calculation in view of its importance in the theory of luminescence.

It would be of interest if the effect of a vacancy in a neighbouring positive ion site could be included in the KCl.Mn calculation. In particular, it might cause a considerable change in the transition probabilities.

Dr. E. Nagy: Although Dr. Williams' calculations correlate well with experiment for KCl.Tl, the theory shows poor correlation for manganese-activated silicates. His theory indicates an absorption band very close to the emission band and also shifts of these bands with temperature which are contrary to experimental evidence. With respect to theory, silicate phosphors appear to form an intermediate class between KCl.Tl and ZnS phosphors.

Author's reply: In reply to Dr. Curie, I agree that at a sufficiently large activator concentration the broadening of the activator levels into a band certainly occurs, but I believe that this occurs only at such high concentrations that the material is no longer an efficient luminescent solid. Experimental support consists in the absence of appreciable dependence of the band width of emission on activator concentration.

In reply to Dr. Butler, it should be emphasized that the configuration co-ordinate model should be applied with caution to systems for which preliminary quantitative calculations have not demonstrated its applicability.

With regard to the splitting of impurity levels, in general the free ion levels are split by electrostatic coupling with the angular momentum of the ion and by exchange repulsion interaction of the activator and the nearest neighbours. The resulting lowest energy level is used in the calculation of luminescence spectra.

Butler's proposal on the reassignment of energy levels for KCl.Tl is not supported by experimental evidence. His statement under (*c*) ". . . the emission is basically the same with 2000 Å excitation as with 2500 Å excitation" is incorrect, for it has been established experimentally that 2000 Å excitation favours 4750 Å emission while 2500 Å excitation favours 3050 Å emission.(2) This confirmed the identification of the 2460 Å absorption and the 3050 Å emission with the $^1S \leftrightarrow {}^3P_0^0$ (6s6p) transitions.(3) Transition probability considerations and the quantitative configuration co-ordinate model support the identification of the 1960 Å absorption and the 4750 Å emission with the $^1S \leftrightarrow {}^1P_1^0$ (6s6p) transitions.(4)

In comparing KBr.Tl with KCl.Tl, as suggested by Dr. Schulman, no important quantitative differences in the theory of excitation and emission are anticipated. The 2610 Å absorption and the 3180 Å emission of KBr.Tl are, almost certainly, the $^1S \rightarrow {}^3P_1^0$ transitions. The slight shift to smaller transition energies compared to KCl.Tl is expected from the greater polarizability of Br^- and consequent greater van der Waals interaction energies. It is attractive to attribute the 3500 Å emission to the $^1P_1^0 \rightarrow {}^1S$ transition just as the 4750 Å emission of KCl.Tl has been attributed to this transition.

Theoretical and practical studies all indicate that the K^+ vacancy in KCl.Mn^{2+} is most probably not associated at a nearest cation site with the Mn^{2+}. With such association, a marked effect on transition probability, but not on transition energy, would be expected.

The emphasis Schulman places on the theoretical determination of transition probabilities is unjustified for KCl.Tl. The $^1S \leftrightarrow {}^3P_1^0$ and $^1S \leftrightarrow {}^1P_1^0$ transitions occur for the free Tl^+ with excellent transition probabilities, and the effect of the lattice perturbations is to enhance these probabilities.

The calculation of the transition probabilities involved in the luminescence of manganese-activated phosphors is an important theoretical problem. We did not identify the transition responsible for the emission of KCl.Mn from the experimental lifetime of the emitting state. The comparison of the results of theoretical calculations of transition energies with experimental spectra revealed that the luminescent emission of Mn^{+2} is due to a transition between states of the $3d^5$ electron configuration differing only in electron spin, whereas calculations assuming that the emitting state had the $3d^44s$ and the $3d^44p$ configurations gave theoretical emission spectra in distinct conflict with experiment. Transition probability considerations were not utilized in the identification of the transition. The transition is a forbidden one so that the millisecond lifetime of the emitting state is not unexpected. The field of the perfect lattice does not appreciably alter the forbidden character of the transition. We now believe the breakdown of the parity selection rule forbidding the transition in Mn^{+2} at a symmetric lattice site arises from asymmetric vibrations of the activator system. This also accounts for the small temperature dependence of the transition probability for emission reported by Kröger.(5) Quantitative calculations of the transition probabilities between states of the $3d^5$ configuration of Mn^{2+} in various phosphors are now in progress.

In reply to Mr. Runciman, regarding the radial charge densities for the 6s and 6p electrons of Tl^+, the inclusion of exchange terms will shift the maxima to slightly smaller radii; therefore, our slightly more localized wave functions obtained with a more approximate core potential may very well be more correct. More significant improvements in the KCl.Tl calculations can be made by direct evaluation of the exact integrals responsible for the repulsion energy of the activator system rather than by approximating them in terms of overlap integrals.

In reply to Dr. Nagy, speculation on the quantitative comparison of theory with experiment for manganese-activated silicates is hardly justified, since no quantitative theoretical treatment of the activator systems of these phosphors has been reported. It is well known that manganese-activated silicates have an absorption band close to the emission band.(6) Also, no appreciable shift with temperature of the peaks of the absorption and emission bands of localized activator systems is predicted by our theoretical investigations.

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Paper 20

Excitation of phosphors by electrons

By G. F. J. Garlick, Ph.D., F.Inst.P., Department of Physics, University of Birmingham

An attempt is made to provide a sound basis for a quantitative theory of cathodoluminescence. Previous theories have neglected the marked scattering of primary electrons by elastic and inelastic collisions, and the effects of this on secondary emission and distribution of secondary electrons responsible for luminescence excitation in the phosphor. Particular attention is given to the detailed processes involved in penetration of the primary particles and to the question of the ultimate limits of cathodoluminescence efficiencies. The latter are shown to be determined by the non-radiative energy transitions of thermal velocity secondary electrons. It appears that the theoretical limit has already been approached in practice.

The extensive study of cathode-ray tube screen characteristics has resulted in the establishment of certain empirical relations between primary electron beam energy and current density and the luminescence output.[1,2,3] The explanation of these relations in terms of fundamental processes in phosphors has been attempted by several workers, notably Fano[4] and later Strange and Henderson,[3] and a critical review of their conclusions has been given previously by the author.[5,6] From modern studies of scintillations in single crystal phosphors, and from studies of thin films of sulphide phosphors, it is clear that the above empirical relations are due to the microcrystalline powder form of the phosphor screens and not to intrinsic luminescence processes in the phosphor; on the other hand, for single crystals and thin films of phosphors the light output varies linearly with electron energy and density except at very high densities (e.g. those produced by slow α-particles).[7] In the treatment of phosphor screen behaviour the usual practice has been to consider separately the data for luminescence *versus* electron energy, and for luminescence *versus* electron beam current density, but this is a rather unrealistic procedure. It is more fundamental to consider electron energy and excitation density in the phosphor. We shall not consider further the previous theories of cathodoluminescence but proceed to a detailed examination of the fundamental processes in the light of evidence from various sources, such as secondary electron emission studies, scattering of β-rays, cathode-ray excitation of single crystal phosphors, and study of single electron trajectories in media of different densities. Such a co-ordination of previously independent fields of research can lead to a much more lucid idea of the cathodoluminescence process.

THE ELECTRON EXCITATION OF PHOSPHORS

We may consider the excitation of luminescence in phosphors by cathode-rays in two stages. The first, to be called the primary process, includes the penetration, scattering and absorption of the primary electrons and the production of secondary electrons which are either emitted from the phosphor or reach thermal velocities in the conduction levels of the lattice. The second stage is concerned with the fate of the thermal velocity electrons, i.e. whether they recombine with luminescence centres to give radiation or lose their energy in non-radiative transitions in other discrete sites in the crystal lattice. The relative occurrence of these alternative ways of return to the ground state will obviously affect the ultimate efficiency of the cathodoluminescence process.

(*a*) *The primary process*

The examination of some studies of secondary emission from solids excited by electrons shows that workers in that field still assume the validity of the Thomson–Whiddington law for the energy *versus* range relation of the primary electrons. The fact that the law holds in some cases is likely to be fortuitous since the path of the primary electron is not clearly defined. It is well known that strong dispersion of the primary beam occurs, particularly in very dense media, so that the true range of the primary electrons is virtually

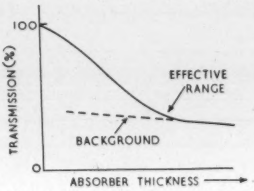

Fig. 1. Typical absorption curve for β-rays in aluminium

indeterminate. This fact is clearly recognized by the nuclear physicist for electrons of much higher energies than those of cathode-ray tube beams although the effect is less in the former case. Fig. 1 shows the absorption curve commonly obtained for absorption of electrons of about 0·1–1·0 MeV in a light metal. It can be seen that even after allowing for background effects the end of the range is not easily deduced

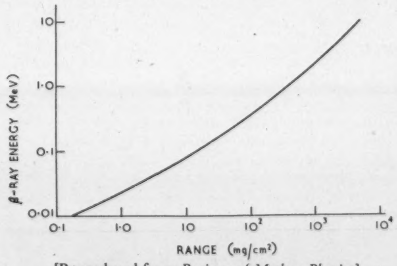

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Fig. 2. Range *versus* energy relation for electrons in aluminium (after Katz and Penfold)

from the curve. Various workers have adopted different methods of estimating the primary electron range and these have been reviewed by Katz and Penfold.[8] After proper corrections to obtain the effective range the collected results were used to plot the range *versus* energy diagram shown in Fig. 2. It can be seen that there is a region between 0·01

and 0·1 MeV where the curve follows the Thomson–Whiddington law approximately, but deviation occurs at the upper end, and, as shown by the experiments of Ehrenberg and Franks,[9] also at the lower end for phosphor crystals. From the curve of Fig. 2 the experimental points were found by Katz and Penfold to fit the following relation over a wide range:

$$R = 412\,E_p^x,$$

where $x = 1{\cdot}265 - 0{\cdot}0954 \log_e E_p$, E_p is the electron energy in MeV, and R is the range in mg/cm^2. At high energies the relation becomes more nearly a linear one. There is little doubt that the complex range *versus* energy characteristics for electrons are due to the presence of strong scattering.

The scattering of the primary electron beam may be either elastic or inelastic, the primary electron producing secondary electrons in the latter case. The occurrence of

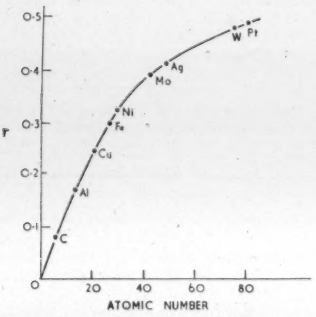

Fig. 3. Variation of back-scattered electrons with atomic number of metal target for 20 keV primary electrons

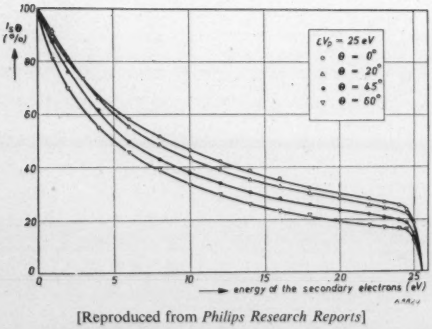

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Fig. 4. Energy distribution of secondary electrons from nickel for various angles of emission and for 25 eV primary electrons (after Jonker)

scattering may be studied by measuring the energy distribution among the electrons emitted from the crystal surface. In the early experiments of Schonland[10] and in more recent work of Palluel[11] it is evident that a large fraction of the primary electrons are scattered back elastically out of the solid, and that this scattering increases with the density of the solid. Fig. 3, deduced from Palluel's data for 20 keV primary electrons, shows the ratio r of the number of fast secondary emitted electrons to the number of primary electrons incident on the crystal surface in relation to the atomic number of the constituent elements, pure metals being used as targets. Fig. 4 depicts Jonker's results for the energy distribution among the secondary emitted electrons for different angles of emergence of the secondaries;[12] in this case a primary beam of only 25 eV energy was used. It is obvious that back-scattering of the primary electrons is very strong for both these cases, and in fact the same is found for high energy β-ray scattering by the elements. The important features of Fig. 3 are (1), the increase of scattering with atomic number with a saturation effect for high atomic numbers due to electron shell screening effects, and (2), the large values possible for the ratio of scattered to original primary electrons. Ehrenberg and Franks[9] demonstrated that the back-scattering is sufficient to prevent "sticking" of the single crystal phosphors at the primary potentials employed, although these are considerably above the sticking potentials of the same phosphors in the form of powder type screens. The increase of back-scattering with atomic number or density of the phosphor has also been beautifully shown by these workers in their photographic records of the luminescence emitting region of the phosphors for various primary beam energies. Except in the case of a plastic phosphor with low density the scattering effect completely obscures the path of the primary electrons and their ultimate range. Elastic scattering effectively lowers the cathodoluminescence efficiency since the primaries emitted from the phosphor in this process represent a considerable fraction of beam energy lost to the luminescence process.

With respect to inelastic scattering which results in secondary electron production, Blanchard and Fano[13] have deduced theoretically that the amount of scattering depends on the fractional energy loss of the primary electrons $(E_0 - E)/E_0$ (where E_0 is the initial energy and E the energy at a later stage), and not on the absolute value of the primary energy to any extent. This would explain the similarity between the scattering curves for electrons of widely different energy and for targets of different atomic number (e.g. Fig. 3), since many of the primary electrons re-emitted have suffered some loss of energy before emerging. With respect to energy loss due to such scattering, Dekker and van der Ziel[14] have obtained the following specific energy loss relation from theoretical considerations:

$$-dE_p/dx \propto E^{-1}.\log_e E_p$$

where E_p is the primary electron energy and x is the depth of penetration in the solid. This obviously differs from the Thomson–Whiddington form in the occurrence of the logarithmic factor. These authors pointed out that the emission of high energy electrons from the surface cannot be due to direct action of the primary electrons on the basis of a free electron model, but follows if the interaction is with bound electrons. In the case of phosphors this latter model would obviously apply. The above relation between specific energy loss and primary electron energy will differ most from the Thomson–Whiddington law when $\log_e E_p$ varies rapidly with E_p, i.e. for low primary electron energies such as those used in the experiments of Ehrenberg and Franks. As they have shown, the scattering of the primary beam is catastrophic as soon as it penetrates into the phosphor. For this reason range deductions are very difficult.

Further evidence in support of the above ideas on the

interaction of primary electrons with the phosphor can be obtained from the study of electron tracks in photographic emulsions and also in cloud chambers. From examination of hundreds of tracks due to fast electrons in electron-sensitive emulsions it is seen that scattering is still a large factor in determining the actual path of the electron. Fig. 5 shows a typical electron track resulting from a nuclear reaction which can be compared with the straight tracks of the heavy particles involved. Fig. 6 shows the tracks of electrons produced in a cloud chamber by passage of an

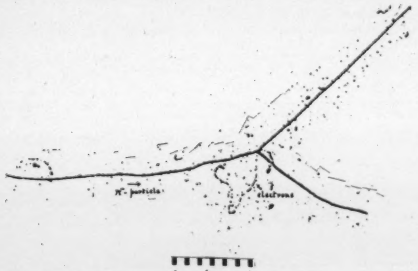

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Fig. 5. Medium energy electron track from nuclear reaction in photographic emulsion (after Powell)

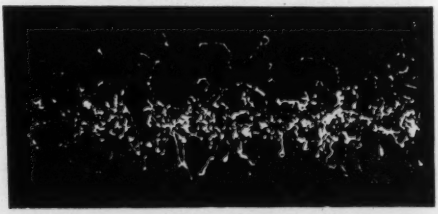

Fig. 6. Electron tracks due to passage of X-rays through a cloud chamber

X-ray beam. From both figures it is evident that violent scattering occurs even at the high energy part of the path, but until the end of the path is approached there is little indication of side tracks due to secondary electrons. However, the sparse population of grains in the emulsion renders the observation of short range secondaries difficult. This is in contrast with the ease of seeing the extent of migration of low velocity secondary electrons by observing the luminescence envelope in a phosphor crystal. There is ample evidence in the results of Ehrenberg and Franks that the resulting volume of excited secondary electrons can have linear dimensions greater by an order of magnitude than the width of the primary beam entering the phosphor, i.e. of the order of 10 μ. This volume is attained both by scattering of primaries and by migration of slow secondaries, the latter process being assumed to be extensive by previous workers.[12,15] The isotropic distribution of secondary electrons assumed by them receives support from the capped sphere type of luminous figure observed by Ehrenberg and Franks.

With respect to the experimental range *versus* energy relations given by the latter workers in Fig. 4 of their paper,[9] we can see that the omission of the zero energy–zero range point allows them to fit the curves to a modified Thomson–Whiddington formula, but this implies a range of some 2 μ at zero energy. This behaviour seems unlikely and it is more realistic to insert the zero of co-ordinates as a point in the results. If this is done then the results for the organic plastic phosphor can be handled in a different way, since the presence of scattering decreases the effective range compared with that for the Thomson–Whiddington relation. For the inorganic phosphors the same applies, except at low primary electron energies where the measured range for the luminous envelope is greater than that expected from the Thomson–Whiddington relation. This can be explained by the extensive diffusion of low energy secondaries in the conduction levels of the crystal lattice, a process expected to be relatively small in the case of the organic phosphor. For this sample the range *versus* energy law is simply $R \propto E_p^{1\cdot4}$, while the results above 10 kV give an index for E_p as low as 0·63 for $CdWO_4$. Such results emphasize the inadequacy of the Thomson–Whiddington law in the case of phosphors.

(*b*) *The secondary process*

We now consider the behaviour of the uniformly distributed secondary electrons within the region of excitation in the phosphor crystal which have thermal velocities and are about to undergo final transitions to their ground states. The previous detailed reshuffling of electron level population means that the electrons under consideration may either recombine with empty luminescence centres or with centres in which their energy is given up non-radiatively. Discussion of these two processes has been given by Schön[16] and others. In the case of a silver-activated zinc sulphide phosphor screen it has been shown by Bril and Klasens[17] that a cathodo-luminescence energy conversion efficiency of 23% can be attained, compared with 21% for excitation by 3650 Å radiation which is a most efficient excitant of photo-luminescence in this phosphor. For the latter excitation the limiting energy efficiency for quantum equivalence, assuming emission at 4700 Å, is about 75%. Thus the radiationless transitions are about twice as numerous as those in luminescence centres. When we take into account the considerable energy lost by emission of back-scattered fast electrons and slow diffusing secondary electrons it would seem that the remaining energy is conserved among the secondaries which slow up and remain in the phosphor. The ultimate cathodo-luminescence efficiency is thus largely dependent on the density of luminescence centres relative to non-radiative centres, as in the case of ultra-violet excitation. However, even with zinc sulphide phosphors the results of Bril and Klasens show that the theoretical limit is being approached.

CONCLUSION

The study of scintillations in single crystal phosphors due to single energetic particles shows a proportionality between light output and energy absorbed in the crystal. The same applies to excitation by a beam of cathode-rays. To explain this in terms of the preceding ideas we must assume that the same fraction of the primary beam energy is lost by secondary emission whatever the primary energy. For single crystals and for energies above about 1 kV the secondary emission current and energy are largely due to back-scattered high energy electrons and this scattering is approximately independent of primary beam energy so that the above assumption

is not unreasonable. In the case of conventional cathode-ray tube screens conditions are rather different. The occurrence of relatively low sticking potentials for phosphor screens must indicate that the inadequate secondary emission is a function of the powder form of the phosphor rather than an intrinsic property. It would be interesting to see experimental results for the dependence of sticking potential on grain size for the same phosphor specimen. As a general observation it may be noted that zinc silicate and calcium tungstate screens show lower sticking potentials than zinc sulphide screens which usually have a much larger grain size.

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DISCUSSION

Dr. A. Bril: (*a*) Dr. Garlick reported that the scattering of fast electrons should be approximately independent of primary beam energy for single crystals and above 1 kV. Measurements of Trump and van de Graaff and of Stehberger,(1) however, show an important increase of the back-scattered high-energy electrons with primary energy for various metals.

It seems that the linear relationship found between light output and beam energy, both for phosphor layers (see discussion of Paper 1) and for single crystals needs further explanation.

(*b*) It is concluded from our measurements with ultra-violet excitation that for the "secondary process" in ZnS.Ag the radiationless transitions are much more numerous than those in luminescence centres. The argument used cannot be applied to cathode-ray excitation. Thus the efficiency of ZnS.Ag does not decrease much if the activator concentration is reduced from 10^{-4} to 10^{-5},(2) and the main loss will therefore take place by the slowing down of the secondary electrons which remain in the phosphor.

To explain the difference in efficiency of various phosphors it would be of great value to know the energy distribution of the secondary electrons, but the present lack of data leaves it uncertain whether the theoretical limit of cathodoluminescence efficiency is being approached.

(*c*) Dr. Garlick remarked that zinc silicate and calcium tungstate screens show lower sticking potentials than sulphide screens; in our experience sulphide screens show charging up at lower voltages than willemite, and the literature gives values of sticking voltages in the same sense.(3)

Dr. V. P. Duggal: In diamonds, much bigger pulses are observed with α-particles than with β-particles. This is contrary to the behaviour of all other organic or inorganic scintillators.

Author's reply: Dr. Bril's reference to back scattering of electrons concerns metals in which case interaction of primaries may be mainly with the free electrons, but for phosphors the theory must assume interaction with bound electrons, a rather different case. However, no detailed theory is yet available.

As regards radiationless transitions the data given by Bril emphasizes the need for more detailed studies of cathodoluminescence. In the case of "sticking potentials" Bril's observations support the view that for powders the value is not a fundamental property of the phosphor but depends on processing and grain size.

Concerning the scintillation response of diamonds we find no marked differences between responses to α- and β-particles of similar energy for green-emitting diamonds. Other types are much less efficient as scintillators and have not been examined in this respect.

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Paper 21

Nonlinearity in photoconducting phosphors*

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The luminescence and photoconductivity of photoconducting phosphors are generally rather complicated nonlinear functions of the exciting intensity, if recombination occurs competitively at two types of centres. Certain properties of several two-centre models have been discussed by earlier investigators, and one model has been examined in detail by Schön. This paper aims at a broader survey of the types of nonlinear behaviour and of the generality of their occurrence with different models.

A family of models is introduced which in a sense exhausts the simple possibilities for two-centre systems. In many cases, the essential features of more complex systems are adequately rendered by the simple models. A suitable method for analysing the models is presented and results are surveyed. Any model with excitation in the fundamental absorption band of the crystal can show emission proportional to the excitation intensity to the power γ over an extended range with $\gamma = 0$, 1/2, 2/3, 1, 3/2, 2, or ∞. Superlinearity is favoured by excitation in the luminescence centres, and sublinearity by excitation in the competing centres. A wider variety of conductivity dependences is found, among which there are cases in which the conductivity decreases with increasing excitation. The results emphasize the great advantage of simultaneous electrical and optical observations on any such system.

The alternate trapping of electrons and holes at impurity or imperfection centres is a recombination process of great importance in many phenomena occurring in the solid state. For example, in photoconducting phosphors the luminescence is due to recombination in a certain type of centre. When competing recombination processes occur in other centres, the competition generally will shift with intensity, giving rise either to sublinear or superlinear luminescence corresponding to a decrease or increase, respectively, of the efficiency of luminescence with increasing intensity of excitation.

The superlinear luminescence of zinc sulphide type phosphors, discovered by Riehl,[1] has been made particularly challenging by the measurements of Nail, Urbach, and Pearlman.[2] They made observations over a large range of excitation intensities and found in one case a high superlinearity with emission proportional to the excitation intensity to the power 3·8. Their measurements were made on zinc cadmium sulphide phosphors containing silver and nickel, and it is a reasonable assumption that the nonlinearity is due to a competition between centres associated with Ag (the emission centres) and those with Ni (the poison centres), the concentrations of both types being subject to control in the preparation of the material. Theories due to Klasens and his collaborators[3] and to Urbach and his co-workers[4] do not explain more than a second-power dependence of emission on excitation. When Roberts and Williams[5] obtained higher powers on the basis of a particular model, it was natural for them to speculate that certain peculiar features of their model, not present in the models of Klasens or of Urbach, were responsible for the high superlinearity. Schön[6] gave a much more complete analysis of another model and found highly superlinear behaviour under certain conditions. The extent to which higher powers in the intensity-dependence result from the distinguishing features of the models of Roberts and Williams and of Schön remains uncertain. It is possible, for example, that the models of Klasens and Urbach would yield higher powers if considered in full generality, that is, without the simplifications introduced by the original authors which served mainly to make the problem mathematically more tractable.

It appeared advisable to attempt a more comprehensive investigation, including a broad range of models and maintaining full generality in their analysis. In this paper, a procedure will be described which makes such a general analysis possible, the general results will be surveyed, and some selected cases will be discussed as examples of a more detailed examination of specific models. It will be shown that, although different types of centres have their special distinguishing characteristics, the overall potentialities of the different types are basically quite similar. In fact, high superlinearity and many other characteristic phenomena are possibilities for almost any model having two competing centres which can be reasonably written down.

BASIC MODELS

The analysis to follow is based upon the four types of centres shown in Fig. 1. The electronic transitions involved are (1) capture of electrons, (2) capture of holes, (3) release of electrons, and (4) release of holes. A solid circle indicates the level is occupied when the crystal is locally neutral, and an open circle that the level is empty. The four centres are all obtained from the centre shown in Fig. 2(*a*) by neglecting one release transition. The exact conditions under which this is valid are easily derived, but roughly, Figs. 1(*a*) and 1(*b*) are valid for low levels and Figs. 1(*c*) and 1(*d*) for high, if the system is appreciably excited. More complex centres are also frequently equivalent, as far as charge storage and

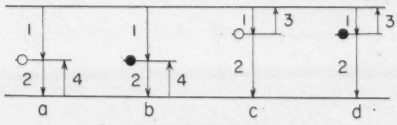

Fig. 1. Basic types of centres

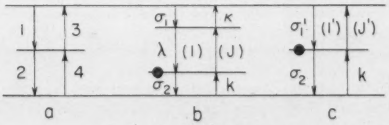

Fig. 2. Equivalent centres

* Communication No. 1618 from the Kodak Research Laboratories.

recombination rates are concerned, to the simple centres of Fig. 1. The centre of Fig. 2(*b*) is equivalent to Fig. 2(*c*) under certain easily derived conditions, including those assumed for it by Roberts and Williams, if

$$J' = J\frac{\kappa}{\kappa+\lambda},\ I' = I - J\frac{\lambda}{\kappa+\lambda},\ \sigma_1' = \sigma_1\frac{\lambda}{\kappa+\lambda} \qquad (1)$$

where J is the excitation and I is the emission rate per unit volume, and the other symbols are rate constants for the transitions as defined in the figure.

Optical excitation in a centre is to be understood as causing the higher-energy release transition, the one not shown in Fig. 1. The emission is always taken to be the high-energy capture transition, although all the reactions in a centre may take place by absorption or emission of phonons.

Each model of a nonlinear photoconducting phosphor must contain two types of centre, one responsible for emission, to be called luminescence or *L*-centres, and the other competing type to be called poison or *P*-centres as they reduce the efficiency of emission. The significance of the following analysis is not restricted, however, to deliberately poisoned phosphors or even to luminescent systems. The four possibilities for each centre generate 16 two-centre models. In a certain sense, the possibilities for constructing models which portray the bare essentials of nonlinear photoconductivity phosphors are thereby exhausted. The 16 models are displayed in Fig. 3 with symbols for the rate constants. The models are represented as eight pairs standing side by side, each the inverse of the other in the sense that the rôles of electrons and holes are interchanged. The analysis of a model and its inverse are identical mathematically, and only one member of each pair need be considered in detail.

Each model can be excited optically in three ways: (1) in the fundamental absorption band of the crystal; (2) directly in the *L*-centre; and (3) in the *P*-centre. When appropriate, the mode of excitation will be indicated by appending the letter *C* (for crystal), *L*, or *P* to the model number, as Model 1*L*, for example.

The incorporation of centres into a crystal will generally cause some shift of the Fermi level from its intrinsic position and will modify the electronic conductivity of the material. In Fig. 1, the centres shown in *b* and *c* introduce low-lying filled levels (hole traps) or high empty levels (electron traps) and will be of relatively little importance for the conductivity. The centres in *a* and *d*, however, have the properties of acceptor and donor centres and will tend to depress or raise the Fermi level, with resulting *p*-type or *n*-type conductivity. All the models except 1, 2, and their inverses contain donor or acceptor centres.

Model 8 and its inverse have both donor and acceptor centres. When this system is left undisturbed, the electrons from the donor centres will go into the acceptor centres so far as possible. Except in the special case when donor and acceptor centres are present in equal numbers, one type of centre will be partially filled. This circumstance, which can have an important effect on the efficiency of luminescence and the kinetics of recombination, will not be discussed further in this paper, although it can be handled by the methods used for the other models.

Many systems undoubtedly contain more than one type of poison centre to compete with the luminescence centre for the excitation energy. When one type of poison is predominant, the system may nevertheless be described by one of the two-centre models; but it must be remembered that the predominance may shift from one poison to another with changing intensity.

METHOD OF ANALYSIS

If the composition of one system from Fig. 3 is specified by giving the concentrations L and P of luminescence and poison centres and the three rate constants for each centre, and if the intensity of excitation of J-photons per unit time per unit volume is known, then one must seek the values of five unknowns: the intensity of emission I; the concentrations of electrons and holes, n and h; and the fractions y and x of *L*- and *P*-centres which have become charged. To answer these questions, five independent equations are available.

The first equation describes the electrical neutrality of the system and contains the four terms n, h, xP, and yL.

$$n + xP = h + yL \qquad \text{for Model 1} \qquad (2)$$

$$n = h + xP + yL \quad \text{for Model 2, etc.} \qquad (3)$$

The second equation defines I as the rate of the lone transition in the *L*-centre.

$$I = n\sigma_2 yL \quad \text{for Model 1, etc.} \qquad (4)$$

It always equates I to a single term involving n or h and y or $(1 - y)$.

The third equation identifies $J - I$ as the lone transition in the *P*-centre.

$$J - I = h\sigma_3 xP \quad \text{for Model 1, etc.} \qquad (5)$$

It involves n or h and x or $(1 - x)$.

The fourth equation expresses the constancy of y and equates the net rate of electron arrival in the *L*-centre from the conduction band to the net rate of release to the lower band. When the excitation is in the *L*-centre, however, the $J - I$ term on one side of the equation is replaced by its equivalent, according to the preceding equation. The fourth equation always involves the rates of three transitions.

$$n\sigma_2 yL = h\sigma_4(1 - y)L - kyL \quad \text{Model 1}C \text{ or } 1P \qquad (6)$$

$$h\sigma_3 xP = kyL - h\sigma_4(1 - y)L \quad \text{Model 1}L \qquad (7)$$

The fifth equation is similar to the fourth but describes the constancy of x and the *P*-centres.

$$h\sigma_3 xP = n\sigma_1(1 - x)P - \kappa xP \quad \text{Model 1}C \text{ or } 1L \qquad (8)$$

$$n\sigma_2 yL = \kappa xP - n\sigma_1(1 - x)P \quad \text{Model 1}P \qquad (9)$$

In order to survey the dependence of the five unknowns on the nine parameters, the following procedure is used: The neutrality, x, and y equations are replaced by one of a group of simpler expressions, each valid under appropriate conditions, then solutions based on all possible combinations of the simple forms are considered. The simple forms of the neutrality equation for Model 1 are:

$$n = h,\ n = yL,\ xP = h, \text{ or } xP = yL \qquad (10)$$

For Model 2

$$n = h,\ n = xP, \text{ or } n = yL \qquad (11)$$

Each form is valid only under certain circumstances. For Model 1, the conditions for $n = h$ are that

$$n \gg xP \text{ and } h \gg yL \qquad (12)$$

The y equation is somewhat different for L excitation than for C or P excitation. In Model 1, for example,

$$y = \frac{h\sigma_4}{k + h\sigma_4 + n\sigma_2} \quad \text{Model 1}C \text{ or } 1P \qquad (13)$$

$$y = \frac{h\sigma_4}{k + h\sigma_4}\left(1 + x\frac{\sigma_3 P}{\sigma_4 L}\right) \quad \text{Model 1}L \qquad (14)$$

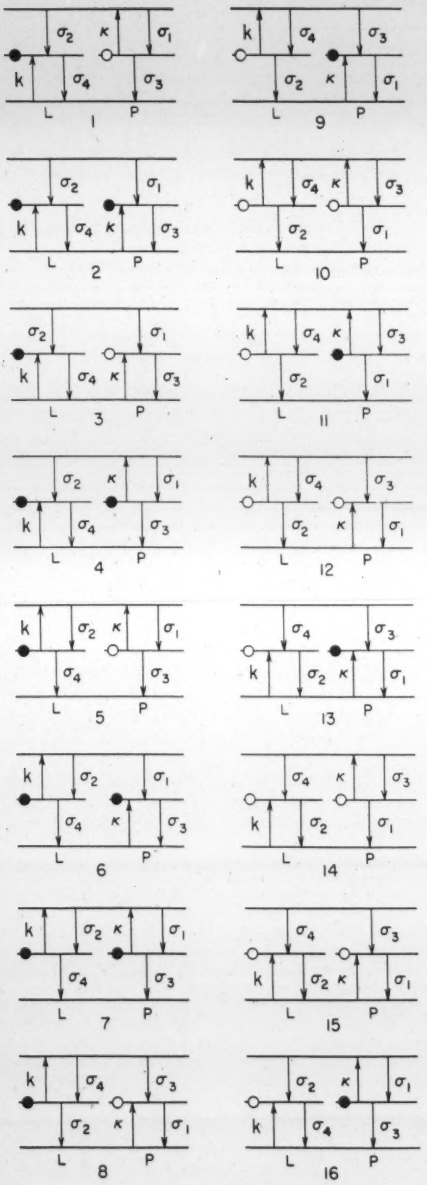

Fig. 3. The basic models

For equation (13) the simple forms are

$$y = h\sigma_4/k;\ y = 1;\ y = h\sigma_4/n\sigma_2 \tag{15}$$

For equation (14) they are

$$y = h\sigma_4/k;\ y = 1;\ y = \left(\frac{h\sigma_4}{k}\right)\left(\frac{\sigma_3 P}{\sigma_4 L}\right)x \tag{16}$$

The x equation is treated similarly.

$$x = \frac{n\sigma_1}{\kappa + n\sigma_1 + h\sigma_3} \qquad \text{Model } 1C \text{ or } 1L \tag{17}$$

$$x = \frac{n\sigma_1}{\kappa + n\sigma_1}\left(1 + y\frac{\sigma_2 L}{\sigma_1 P}\right) \qquad \text{Model } 1P \tag{18}$$

These give as simple forms

$$x = n\sigma_1/\kappa;\ x = 1;\ x = n\sigma_1/h\sigma_3 \qquad \text{Model } 1C \text{ or } 1L \tag{19}$$

$$x = n\sigma_1/\kappa;\ x = 1;\ x = \frac{n\sigma_1}{\kappa} y\frac{\sigma_2 L}{\sigma_1 P} \qquad \text{Model } 1P \tag{20}$$

In Model 1 there are approximately $4 \times 3 \times 3 = 36$ cases corresponding to four forms of the neutrality equation and three each for the x and y equations. The case $xP = yL$ must be omitted, however, when $x = y = 1$. Occasionally, as in Model 2, only three forms of the neutrality equation are involved. On the other hand, four forms for x or y will be involved if it is necessary to have accurate expressions for $1 - y$ in addition to y (or $1 - x$ in addition to x). In Model 3, it is necessary to have x for the neutrality equation (at least when $xP = h$ or when $xP = yL$) and simultaneously an accurate form for $1 - x$ for use in $J - I = n\sigma_1(1 - x)P$. For Model $3C$ or $3L$,

$$x = \frac{n\sigma_1 + \kappa}{n\sigma_1 + \kappa + h\sigma_3} \text{ and } 1 - x = \frac{h\sigma_3}{n\sigma_1 + \kappa + h\sigma_3} \tag{21}$$

The simple forms are

$$x = 1,\ 1 - x = h\sigma_3/n\sigma_1;\ x = 1,\ 1 - x = h\sigma_3/\kappa; \tag{22}$$
$$x = n\sigma_1/h\sigma_3,\ 1 - x = 1;\ x = \kappa/h\sigma_3,\ 1 - x = 1.$$

As a complete example of a single case, consider Model $1L$, with $xP = h$, $y = 1$, $x = 1$, for neutrality, y, and x equations.

$$\text{Then } y = x = 1,\ h = P,\ J - I = \sigma_3 P^2,\ I = n\sigma_2 L \tag{23}$$

Now if $J \gg I$, then $J = \sigma_3 P^2$. This is a case where I and n increase discontinuously while J is constant, i.e. infinite superlinearity occurs. The conditions for validity of this case are

$$xP \gg n,\ h \gg yL,\ n\sigma_1 \gg \kappa,\ n\sigma_1 \gg h\sigma_3,$$
$$h\sigma_4 \gg k,\ kL > h\sigma_3 xP \tag{24}$$

Using expressions (23), we may rewrite the above conditions and separate them into two groups. The first restricts the constitution of the system.

$$\left.\begin{aligned} &P \gg L,\ P\sigma_4 \gg k,\ P \gg \kappa/\sigma_1,\ kL > \sigma_3 P^2 \\ &\frac{\sigma_3}{\sigma_1} \ll 1 \text{ and for } J \gg I \text{ also } \sigma_1 P \gg \sigma_2 L \text{ and } \sigma_1\sigma_3 P^2 \gg \sigma_2 L\kappa \end{aligned}\right\} \tag{25}$$

If the constitutive inequalities are satisfied only weakly, the behaviour will only approximate to that typical of the case. The second group restricts the intensity.

$$P \gg n,\ \frac{P\sigma_4}{\sigma_2} \gg n,\ \frac{\kappa}{\sigma_1} \ll n,\ \frac{P\sigma_3}{\sigma_1} \ll n \tag{26}$$

$h \gg n$ whenever this case is realized.

It is obvious that the conditions just derived are necessary and that, if they are satisfied, a solution of the original five equations is known. The problem of the sufficiency of the conditions is then equivalent to asking if the original equations have a unique solution. It is usually easy to demonstrate that the equations have a unique solution for positive values of the unknowns and for x and y less than 1.

In the case just cited, if the constitutive parameters of a system are known and they satisfy the inequalities, then when $J = \sigma_3 P^2$, the case will be realized. By selecting the most restrictive lower and upper bounds to n, it is not difficult to determine the neighbouring cases for lower and higher intensities, that is, *to establish the intensity sequence of cases for a system of known constitution.*

By the application of this method, one can obtain for each model complete descriptions of a large number of special types of limiting behaviour and get thereby a good survey of possible forms of behaviour for each model and the conditions under which they will occur.

RESULTS

For all models, it is possible to select those cases which form the beginning of intensity sequences and for which all the intensity conditions have the form $J \ll$ (some combination of parameters). There are two types of cases which terminate intensity sequences. In the first, all the intensity conditions have the form $J \gg$ (something). The second type, which occurs only when the excitation is in one of the centres, has an upper limit to J expressed by a condition $J \leqslant$ (something). When J attains the finite limit, however, all the centres in which the excitation occurs will be in that charge state which makes their absorption for the exciting radiation vanish. The finite upper limit on J would be realized, in practice, only for infinite incident intensity of exciting radiation, and this case will terminate the intensity sequence. The significance of the finite limit is easily understood physically by considering, for example in Model 1*L*, that $J - I$ is limited by the rate at which electrons are thermally raised from the lower band into the centres, namely $J - I = kL$. This form of high-intensity saturation is quite distinct from that usually discussed, in which the saturation of a centre is due to the finite lifetime of the excited emission state.

With regard to the nonlinearity of emission, the simplest results are obtained where the excitation is produced in the fundamental absorption band of the crystal so that J may be taken as proportional to the incident intensity. Then, if I is proportional to J^γ, cases with $\gamma = 0$, 1/2, 2/3, 1, 3/2, 2, and ∞ are found for Models 1*c* to 7*c* inclusive and their inverses. For each γ in the above list, $1/\gamma$ also occurs. There is thus a balance between sublinearity and superlinearity expressing the fact that the *L*- and *P*-centres compete on an equal footing when the excitation is produced directly in the crystal lattice.

Excitation in the *L*-centres favours superlinearity, and excitation in the *P*-centres favours sublinearity. For example, in Model 1*L* cases are found with $\gamma = 0$, 1/2, 1, 3/2, 2, and ∞. The sublinear power, 2/3, is missing. Furthermore, the values of 0 and 1/2 occur only in cases where y is approximately 1 and are thus always accompanied by the emptying of the absorbing *L*-centres. To change from J to incident intensity of excitation, one must take into account that the absorption will be proportional to $1 - y$. With Model 1*P*, cases are found for $\gamma = 0$, 1/2, 2/3, 1, 2, and ∞. The power 3/2 is missing and 2 and ∞ occur only when x is approximately 1.

The model proposed by Urbach[2] was 1*L*, and the model of Roberts and Williams[5] is equivalent to this in the cases they discussed because of the relations mentioned in connexion with Fig. 2(b). Application of the present method to Model 1*L* reveals several cases of high superlinearity ($\gamma = \infty$), in all of which $n \ll P$ in the neutrality equation and $x = 1$, but y may take any simple form. If one goes back to the original five equations and uses only the relations $x = 1$ and $n \ll P$, it will be found that h, y, $J - I$ are constant, while I is proportional to n. If conditions are such that $J \gg I$, the behaviour will be highly superlinear. Roberts and Williams only described the case in which $y = h\sigma_4/k$. The case in which $y = 1$ is rather artificial because of the important distinction between J and incident intensity, but the case in which $y = h\sigma_3 P/kL$ is a significant addition. The third centre considered by Roberts and Williams, an electron trap, introduces no new phenomena as long as it behaves as they assumed.

The dependence of electronic conductivity on J, that is, photoconductivity, is quite different from that of I and is more variable from model to model. Systems containing only one type of the centres shown in Fig. 1 always have linear emission with $J = I$, but their electronic conductivity varies as J^γ with $\gamma = 1/2$ or 1 for the nonsemiconductors and with $\gamma = 0$, 1/2, or 1 for semiconductors. Superlinear dependences may occur for the minority carrier, however. The two-centre models preserve this tendency towards sublinearity in showing a greater variety of sublinear cases than of superlinear, but the latter do occur.

For the conductivity in Model 1*C*, the values $\gamma = 0$, 1/3, 1/2, 2/3, 1, and ∞ occur. Each case can exist with either electrons or holes in the majority. From Model 1*L*, or 1*P*, the values are $\gamma = 0$, 1/4, 1/3, 1/2, 2/3, 1, and ∞.

For the conductivity in Model 2*C*, $\gamma = 0$, 1/3, 1/2, or 1. Whereas Model 1*C* is qualitatively symmetrical with respect to electrons and holes, 2*C* contains only hole traps; and holes are always the minority carriers.

For the conductivity in 3*C*, $\gamma = 0$, 1/4, 1/3, 1/2, 1, 3/2, 2, and ∞. The values for 4*C* are the same as for 2*C*, and again the minority carriers are always holes. For 5*C*, $\gamma = 0$, 1/3, 1/2, 2/3, 1, 2, and ∞. For 6*C* and 7*C*, the powers are again the same as for 2*C*. Of course, the rôles of electrons and holes are completely interchanged in the inverse models.

A new conductivity phenomenon is illustrated by Model 3*L*. This model, although a *p*-type semiconductor, has the same γ-values for luminescence as 1*L*. The conductivity values, however, are $\gamma = 0$, 1/4, 1/3, 1/2, 2/3, 1, ∞, $-1/2$, -1 and $-\infty$, where the negative numbers are to be noted particularly. When γ is negative, the conductivity decreases with increasing J. In the negative cases, the majority carriers are always holes. In a typical intensity sequence, the conductivity for very low J will be approximately the normal dark value. At higher intensities, one or more of the negative cases can occur and the conductivity decreases. For still larger J values, other cases may occur and the conductivity begins to rise. This photoconductive negative effect is entirely electronic in nature, whereas the negative effect observed by West[7] is described as a reduction of a dark ionic conductivity.

Much detailed information, including correlations between luminescence and conductivity, can be obtained by the straightforward, though somewhat tedious, methods described in this paper.

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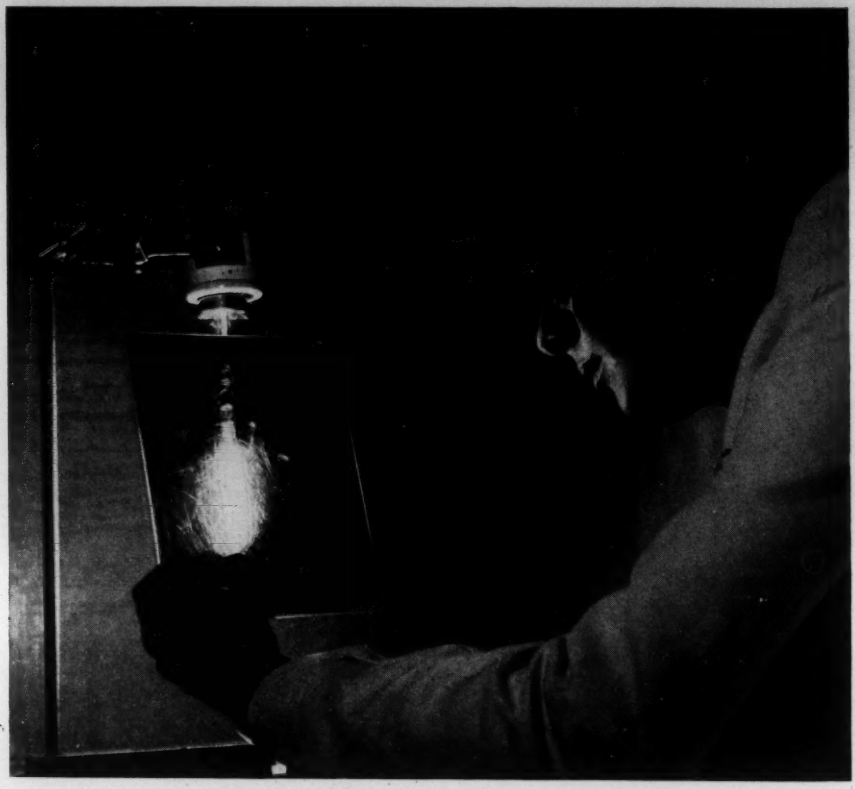

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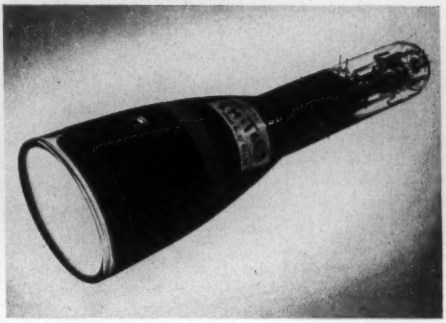

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